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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

METALLOCHEMISTRY AND SOME OF ITS PROBLEMS

I. I. Kornilov

(Paper read at a General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, September 27, 1956)

1. Metallochemistry as a Science

The systematic investigation of chemical interaction between metals began at the end of the last century. Kurnakov's first paper "Mutual Compounds of Metals", which was published in 1899 [1], prompted numerous investigations in this direction: we must mention investigations on equilibria in metal systems by Baikov [2], Stepanov [3], and Urazov [4]. The investigations of Kurnakov, Baikov, and others on metal systems greatly interested Mendeleev in connection with his work on the theory of solutions and chemical compounds [5]. Work of similar character was also being carried out abroad: we must mention the investigations of Tammann in Germany [6], Austen in Great Britain [7], and le Chatelier in France [8]. Further investigations of the phase diagrams of metal systems developed in association with the general progress of physicochemical analysis, which was founded by Kurnakov [9].

In the development of investigations on the interaction of metals, Mendeleev's periodic law was of great importance. The study of alloys, developed on the basis of the periodic law and equilibrium theory, was gradually transformed into a scientific discipline, which has now been called "metallochemistry".

Modern metallochemistry developed from chemical metallography, which was first given this name by Kurnakov in 1936 [10]; it was later called alloy chemistry by Ageev [11]; and it has now been unified under the general term of metallochemistry [12]. Metallochemistry is developing in a field bordering on general and inorganic chemistry, physical chemistry and physicochemical analysis, physics of solids, metal physics, and crystal chemistry.

The general problems of metallochemistry, which became defined in the course of its development, may be expressed in the following form: "study of chemical interaction of metal elements among themselves, or with nonmetals when solutions or compounds containing bonds of a metallic character are formed, and the establishment of the laws of the formation and the structure of an extensive class of solutions and metallic compounds".

Metallochemistry is concerned with peculiar interactions between atoms which results in the formation either of solid solutions or of metallic compounds of variable or constant composition. Moreover, such compounds are not generally in accordance with the theory of valency. This characteristic distinction of metallochemistry – the formation of metallic compounds that do not conform with valency theory – makes it richer and of greater content than the chemistry of nonmetallic compounds.

There is no class of inorganic – and still less, organic – substances in which the propensity for isomorphous substitution or inclusion of foreign atoms within the crystal lattice is so strongly marked as the class of solid metallic solutions. These solid solutions are formed also between metallic compounds [13]. In this respect solid solutions of metals and metallic compounds can be compared only with natural inorganic compounds – minerals – in which we again find a considerable tendency for isomorphous substitution in some compounds, e.g. oxides, sulfides, and silicates.

In many respects there is an analogy between metallic solid solutions and solid solutions of minerals. For example, many iron meteorites are solid solutions of iron with nickel and cobalt. Similar solid solutions can

be obtained also synthetically – by melting these three metals together. Taking the solid solutions of carbides of iron-group metals $(FeCoNi)_3C$ (the mineral cohenite) and of the corresponding phosphites $(FeCoNi)_3P$ (the mineral schreibersite) as examples, we may point to the analogy between these meteoric minerals and similar solid solutions of carbides and phosphides prepared synthetically under laboratory conditions.

We may regard the subject matter of metallochemistry as the study of three basic reactions between metals:

1. The reaction of the formation of solid solutions between metals and between metallic compounds.

2. The reaction of the formation of metallic compounds and their gradual transition into compounds of the semiconductor and ionic types.

3. Crystallochemical reactions proceeding in solid metal systems.

The last includes the formation of compounds from solid sulutions during their cooling or dissociation and their transition into solid solutions when heated; transformations in limited solid solutions of metals; and eutectic transformations associated with polymorphous modifications of pure metals and metallic compounds. Crystallochemical reactions include also surface interaction of metals and alloys with the external medium – oxidation, solution, diffusion, and other processes.

The above-listed reactions in metal systems can be studied both by the methods of homogeneous and heterogeneous equilibrium and also by kinetic methods.

2. Formation of Metallic Solid Solutions

The ability of metals to form an extensive class of solid solutions arises from their positions in the periodic system, the similarity in the electron structures of the atoms, the small differences in atomic diameters, and isomorphous crystalline structure (this last is essential for the formation of continuous solid solutions). Various investigators have drawn attention to this situation [14-16].

The explanation of the ability of metals to form solid solutions can be seen particularly clearly by an examination of the relation of the atomic diameters of elements to their atomic numbers. As can be seen from Fig. 1, all the elements of the periodic system fall into three groups according to the magnitudes of their atomic diameters. One group embraces a large number of metallic elements having medium atomic diameters varying approximately from 2.2 A to 3.0 A. The other two groups occupy the extreme positions. One of these is a small group and consists mainly of nonmetals of small atomic diameter; it occupies the lower part of Fig. 1. The other contains alkali and alkaline-earth metals and some metals of the subgroups (In, Sn, Sb, Tl, Pb, Bi); these have large atomic diameters, differing greatly from those of the elements of the other two groups. The relative atomic diameters of elements in many cases determines the possibility or impossibility of the formation of metallic solid solutions.

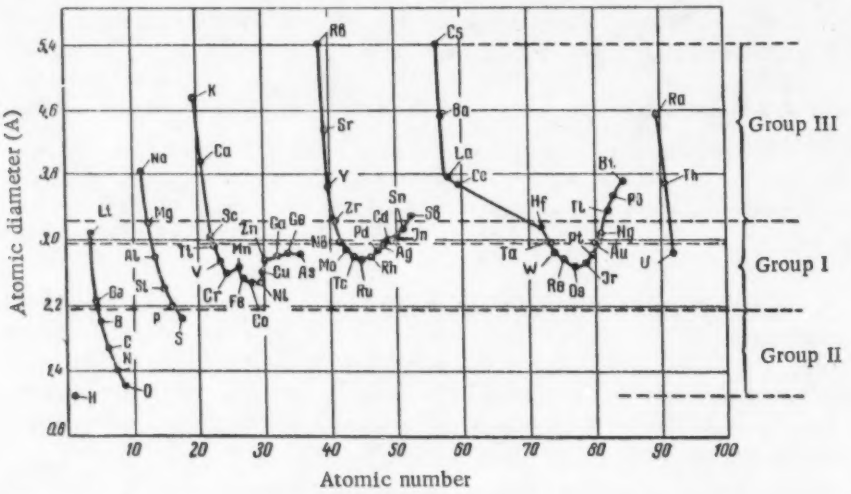

Fig. 1. Relation between atomic diameters of elements and atomic numbers.

Metals of the first group have the greatest tendency to form continuous solid solutions of the substitution type with one another. Nonmetals of small atomic diameter in the lower part of Fig. 1 are able to form only limited solid solutions of the inclusion type with metals. Metals of the third group with large atomic diameters have the least tendency to interact with metals of the main groups of the periodic system. For elements that differ greatly in atomic diameter it is characteristic that they are not only incapable of forming solid solutions or compounds, but are also immiscible in the liquid state.

The formation of solid solutions has been examined in its relation to relative atomic diameters for copper [15], aluminum [17], iron [16], nickel [18], chromium [19], and titanium [20]. On the basis of these investigations it may be considered that the formation of solid solutions of metals is determined by the positions of the metals with respect to the groups of the periodic system. This is shown in the interaction of metals of Group IV (Ti-Zr-Hf), Group V (V-Nb-Ta), Group VI (Cr-Mo-W), and various metals of Groups VII and VIII, the exceptions being metals of nonisomorphous crystal structure (Mn with Re, Fe with Ru, and others).

The tendency to form continuous solid solutions is found also in other groups. For example, in the alkali-metal group continuous solid solutions are formed between analogs, i.e. potassium and cesium, cesium and rubidium; similar continuous solid solutions are formed in the systems germanium-silicon, arsenic-antimony, and antimony-bismuth.

The tendency for the formation of solid solutions of metals within a period diminishes as we pass from analogous pairs to pairs differing greatly in properties, i.e. it changes progressively as we pass from one group to another. The behavior corresponds to the change in chemical properties. For example, for Ni this diminution in solubility can be represented by the following series:

$$Ni \rightarrow Co \rightarrow Fe \rightarrow Mn \rightarrow Cr \rightarrow V \rightarrow Ti \rightarrow Sc \rightarrow Ca \rightarrow K.$$

With Co, Fe, and Mn nickel forms continuous solid solutions, with Cr, V, and Ti only limited solutions, and with Ca and K there is no interaction at all. For titanium, a metal of Group IV, the position is reversed. The solubility of elements in titanium diminishes along the following series:

$$Ti \rightarrow V \rightarrow Cr \rightarrow Mn \rightarrow Fe \rightarrow Co \rightarrow Ni.$$

At high temperatures titanium forms continuous solid solutions with V and Cr, but with Mn, Fe, Co, and Ni it forms only limited solutions. Moreover, the limiting concentration of the metals of limited solubility in titanium also diminishes progressively from Mn to Ni, as shown in a review paper [21].

For example, if we examine the limiting solubility of metals (from Cr to Ni) in the high-temperature modification of β-titanium, we obtain the following results: Cr gives continuous solid solutions with β-Ti, but the solubilities of Mn, Fe, Co, and Ni in β-Ti are 30, 20, 15, and 11 atom percent, respectively.

As will be seen, as the element becomes further removed from titanium in the periodic system, its solubility becomes limited and the limiting concentration in the solid solution then gradually falls. The correctness of this statement can be confirmed for the case of other metals, e.g. for the interactions of chromium and of its Group VI analog, molybdenum. Fig. 2 indicates the formation of continuous and limited solid solutions of chromium with various metals – these metals being either in Group VI or in the vicinity of chromium with respect to groups and periods.

3. Formation of Metallic Compounds

As metallic elements become further removed from one another in the periodic system and the difference in their chemical properties increases, not only does the tendency for the formation of solid solutions diminish, but there is an increased tendency for the formation of metallic compounds of constant or variable composition without any signs of valency relationships.

Many papers [22-25] have been devoted to the question of the formation of metallic compounds and their classification; they enable us to reach some general conclusions.

It has now been found that, even in the most ideal types of solid solutions, such as those formed by analogs (silver-gold, chromium-molybdenum, cobalt-nickel, etc), sensitive methods of investigation show the presence

of compounds resulting from interaction between the electrons of these metal-analogs. For example, it has been shown by the galvanomagnetic method [26] that in many of the continuous solid solutions referred to above chemical compounds of various stoichiometric compositions are formed.

The formation of metallic compounds can be shown for other metals. Figure 3 refers to some series of nickel compounds and shows the relation between the temperatures of formation of the compounds and the position of the metal interacting with nickel in the periodic system.

As can be seen from Fig. 3, the temperature of formation of a nickel compound is the higher, the further the second metal is removed from nickel. The formation temperatures of these compounds rise in the following order:

$$Ni_3Fe \rightarrow Ni_3Mn \rightarrow Ni_3Cr \rightarrow Ni_3V \rightarrow Ni_3Ti.$$

The first four compounds (from Ni_3Fe to Ni_3V) are formed from solid solutions, and the compound Ni_3Ti is formed in the crystallization of a liquid solution. Approximately the same order is found for the change in temperature of formation of compounds of nickel with metals of the fifth and sixth periods (Fig. 3).

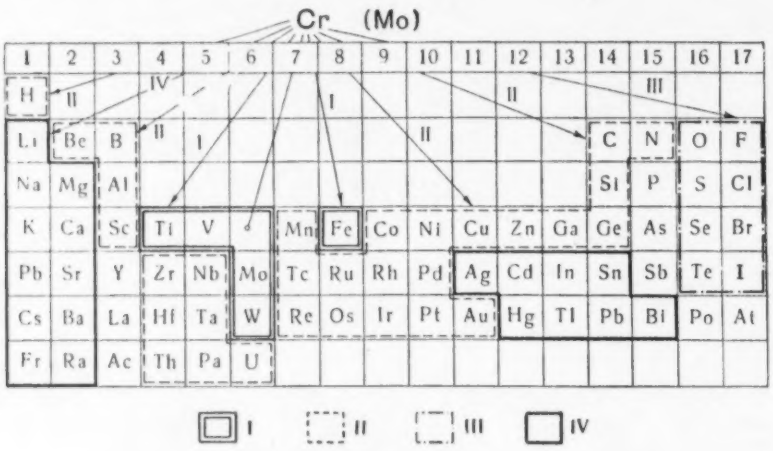
Cr (Mo)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
H Li Be B Na Mg Al K Ca Sc Pb Sr Y Cs Ba La Fr Ra Ac
Ti V Zr Nb Mo Hf Ta W Th Pa U
Mn Fe Co Ni Cu Zn Ga Ge As Se Br Tc Ru Rh Pd Ag Cd In Sn Sb Te I Re Os Ir Pt Au Hg Tl Pb Bi Po At
C N O F Si P S Cl
I II III IV

Fig. 2. Interaction of chromium with other elements: I) continuous solid solutions; II) limited solid solutions with metallic compounds; III) ionic compounds without solid solutions; IV) no interaction.

The temperature of formation of a compound characterizes its thermal stability and in some measure reflects the stability of the chemical bond in the compound. This last property can be characterized also by the heat of formation of the compound, as will be shown below for compounds of magnesium.

TABLE 1

Compounds of Magnesium with Elements of the 5th, 7th, and 9th Rows.

Row of elements	Elements and magnesium compounds	Compositions of compounds					
5	Elements	Cu	Zn	Ga	Ge	As	Se
	Compounds	Mg_2Cu	MgZn	Mg_3Ga_2	Mg_2Ge	Mg_3As_2	MgSe
7	Elements	Ag	Cd	In	Sn	Sb	Te
	Compounds	MgAg	MgCd	Mg_3In_2	Mg_2Sn	Mg_3Sb_2	$MgTe$
9	Elements	Au	Hg	Tl	Pb	Bi	Po
	Compounds	MgAu	MgHg	Mg_3Tl_2	Mg_2Pb	Mg_3Bi_2	MgPo?

It may therefore be considered that the tendency to form metallic compounds and their stability increase as the difference in chemical properties of the interacting metals increases. We then observe a gradual transition from compounds having bonds of a metallic character, through compounds having semiconductor properties, to compounds of the ionic type. This position is particularly clear in the case of the compounds of magnesium, a typical Group II metal, with elements of the B subgroups in the 5th, 7th, and 9th rows of the periodic system. Here we find the formation of a series of metallic compounds, and as the chemical difference between these elements and magnesium increases a transition to ionic compounds is observed. These magnesium compounds are shown in Table 1. The same sequence is found for the reduction of the solubility of these elements in magnesium in the solid state.

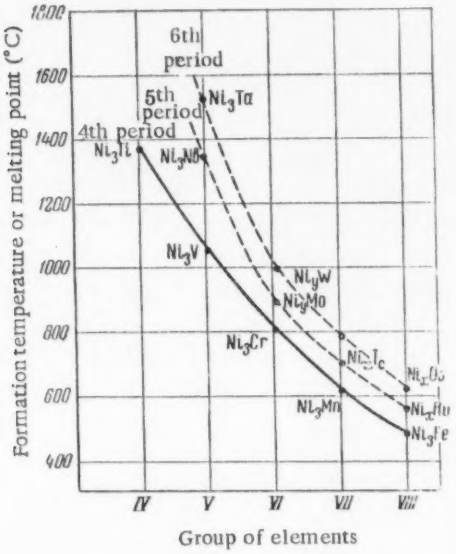

Fig. 3. Metallic compounds of nickel with elements of the 4th, 5th, and 6th periods, and their formation temperatures.

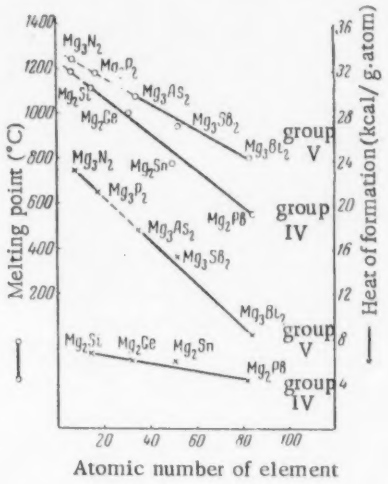

Fig. 4. Temperatures (– O –) and heats (··· x ···) of formation of compounds of magnesium with Group IV and V elements.

As is well known, magnesium, in its interaction with elements close to it in the periodic system (Cu, Ag, Au, Zn, Cd, and some others), is able to form not only typical metallic compounds, but also limited solid solutions. As the elements become further removed from the magnesium group, their tendencies to form solid solutions with magnesium diminish, but there is an increase in the tendency for the formation of compounds with a valency ratio of atoms until we finally arrive at a bond of ionic character (MgSe, MgTe, etc.).

It is very characteristic that a group of elements of the metalloid type (Ge, As, Sb, etc.) show only a slight tendency to form solid solutions with typical metals, including magnesium, but have a great tendency to give compounds of the semiconductor type; these include compounds such as the arsenides and stibides of typical metals, many of which are semiconductors. Mg_3As_2, Mg_3Sb_2, NiAs, CoAs, CoSb, and others are compounds of this type. A review of a large group of such compounds is given in the papers [27] and [28].

The temperatures of formation of magnesium compounds, and also their heats of formation, are related to the positions of the second elements in the periodic system. For comparison purposes we represent these two properties of compounds of magnesium with Group IV and V elements in Fig. 4. As will be seen from the series of straight lines representing the changes in the temperatures and heats of formation of these compounds, there is a definite correspondence between these two properties. Maximum temperature of formation corresponds to maximum heat of formation.

Of the nonmetals, two groups can be distinguished, and one of these consists of elements of small atomic diameter (boron, carbon, nitrogen, and in some respects oxygen) which are able not only to form limited solid solutions of the inclusion type, but to give also compounds in which the bonds are metallic or transitional

TABLE 2

Continuous Solid Solutions of Systems of Metallic Compounds

Compounds of typical metals	Carbides	Semiconductor compounds
Cu_3Au—Cu_3Pt	Fe_3C—Mn_3C	FeAs—NiAs
Ni_3Fe—Ni_3Mn	Fe_3C—Ni_3C	NiS—CoS
Ni_3Ti—Ni_3Nb	Ni_3C—Mn_3C	NiAs—CoAs
Ni_3Nb—Ni_3Ta	Fe_3N—Ni_3N	NiAs—CoSb
Ni_3Ti—Ni_3Ta	TiC—ZrC	NiSb—CoSb
Fe_3Al—Ni_3Al	TiC—HfC	PbSe—PbTe
FeCr—FeV	ZrC—HfC	Bi_2S_3—Sb_2S_3
FeCr—CoCr	TiC—VC	HgSe—HgTe
FeAl—NiAl	TiC—NbC	HgTe—β-HgS
NiAl—CoAl	VC—NbC	HgSe—β-HgS
FeAl—CoAl	NbC—TaC	InAs—InSb
		InSb—GaSb
And others	And others	And others

between metallic and ionic in character. Compounds such as borides, carbides, and nitrides are typical metallic compounds, and oxides are semiconducting or ionic compounds. Many investigations have been devoted to this class of compounds [29-31].

The nonmetals silicon and phosphorus, which have atomic diameters close to those of many metals, also belong to the group of elements that form limited solid solutions and metallic compounds of the silicide and phosphide type with metals.

The second group of nonmetals – Groups VI and VII (sulfur and halogen groups) – contains elements which are unable to form solid solutions with metals, but have a great tendency to form typical ionic compounds. It is here characteristic that the lower compound of the type M_XR_Y (R = S, Se, Te) has metallic properties (e.g. NiS), and compounds richer in R (e.g. NiS_2) have semiconductor properties. Metal halides are typically ionic.

Many metallic and ionic compounds are able to form continuous or limited solid solutions. The tendency for the formation of solid solutions between compounds is determined by certain conditions, which were considered in the papers [32]– [37]. This work not only explains the experimentally established facts concerning the formation of such solid solutions, but makes it possible to predict their formation in systems not yet studied. Table 2 lists some examples of the formation of continuous solid solutions between metallic compounds of various types.

4. Some Tasks of Metallochemistry

From a consideration of the most important aspects of modern metallochemistry, we can determine what tasks it must now undertake.

1. On the basis of the application of Mendeleev's periodic law we must develop the further study of the laws governing the formation of solutions and compounds of various classes by metals. Concepts concerning the formation of solid solutions by metal-analogs can be extended to the problem of the formation of solid solutions of compounds having bonds differing in degree of metallic character. It is important also to apply these laws in the prediction of the types of equilibrium diagram given by hundreds and thousands of simple and complex metal systems which have been studied very little or even not at all.

2. The development of the theory of the chemical structure of metallic solid solutions and compounds. Investigations on the electronic structure of these systems and on the nature of the chemical bond in alloys must be greatly extended. It is particularly important to make the fullest application of sensitive galvanomagnetic [22], optical, X-ray-spectrum [38], radiochemical [39], and other methods in the determination of the character of the bond in metallic compounds of various types.

3. In connection with the second task, there must be considerable development in the study of the transition from a metallic bond to an ionic, salt-forming bond through a series of intermediate metallic compounds of the semiconductor type. Metallic compounds of various classes provide an extremely promising basis for the investigation of the question of gradual and sudden transitions from one type of chemical bond to another [40].

4. The study of the relation between the character of the chemical bond and the crystal structure in solid solutions and metallic compounds. At the present time we can speak only of a few regularities observed in the structures of binary metallic compounds, which have been considered in several papers [22-25, 29-31, 41, 42].

It should be noted that study of ternary and more complex metallic solid solutions and compounds, which are probably not less widely found than binary systems, has scarcely begun. This part of the work is particularly important owing to the fact that alloys of practical importance are based on ternary, quaternary, and more complex metal systems. Little studied structural questions include the question of the structure and the character of the bond in a whole series of metallic refractory compounds such as borides, silicides, carbides, and nitrides. Much work has recently been devoted to these questions [43].

5. Further development of work on equilibria in metal systems. As well as continuing work on phase diagrams of systems based on the better known metals such as iron, nickel, and aluminum, we must study equilibrium systems based on metals which should be introduced extensively into practice, e.g. germanium and silicon, titanium and zirconium, vanadium and niobium, chromium and molybdenum. Full advantage must be taken of the possibility of predicting the existence of various concrete systems on the basis of the theory of the formation of metallic solutions and compounds. It is particularly important here to investigate multicomponent metal systems having the greatest importance for the basis of practically valuable alloys [44].

6. The task of investigating the interaction of metals in multicomponent systems is closely associated with the purely chemical investigation of the selective separation of metallic phases in such complex systems. If the question of the individualization of these phases is resolved, then questions concerning the existence of limiting concentrations of multicomponent solid solutions of metals and of metallic compounds will be greatly clarified.

7. The investigation of the reactions by which metallic compounds are formed, the kinetics of various transformations in the solid stage, and reactions on the surface of alloys (diffusion processes, oxidation, etc.). The fact that these processes occur in a crystalline medium (for which reason they are called crystallochemical reactions) makes them complex in character [45]. These processes, which are mainly of an atomic and not molecular character, may proceed, depending on conditions and on the chemical structure of the alloy, instantly, rapidly (martensite transformations), or over a period of hundreds, thousands, or millions of hours, extending right on to geological periods of time (low-temperature breakdown of supersaturated solid solutions). In these processes, chemical peculiarities are revealed by the appearance of singular points in diagrams of rate of transformation against composition [46].

8. The study of reaction kinetics in solid metals is associated with the task of studying the reactivity of alloys in the chemical sense. Chemical passivation phenomena are found in solid solutions of metals, the reactivity being lost right up to high temperatures so that the system acquires a property of practical importance – heat-stability. On the other hand, in metallic compounds high reactivity often develops [47, 48]. This is particularly characteristic for those intermediate states of compounds corresponding to various stages in the formation and transformation. It would appear that under these conditions, in which there are activated atoms that are to some extent free and are not at the equilibrium points of the crystal lattice of the substance undergoing transformation, these atoms become more chemically reactive than in compounds or solid solutions in an equilibrium state. These view are confirmed by the high catalytic activity of various metallic compounds (with an ordered structure) as compared with the low activity of solid solutions (with a disordered structure) [49]. The study of these phenomena in alloys comprises an important section of metallochemistry.

9. The study of the relation between the chemical structure of alloys and their properties is an important task within the framework of the theoretical study of the relationship between the properties and structure of matter which occupied the minds of our great scientists, including Mendeleev, Butlerov, and Kurnakov. Of particular importance for metallic solutions and compounds are their mechanical properties, which determine their practical application as constructional materials.

The knowledge of the fundamental laws determining the relationship between composition, structure, and properties of alloys is bound to give a guide to the synthesizing of new metallic substances having predetermined

properties. These problems include the preparation of new metallic materials of high electrical conductivity and others of high resistivity, even to the extent of being dielectrics; others are required of high chemical stability, of high chemical activity (catalysts), of high plasticity (ability to become deformed), and of high hardness and strength (including high strength at high temperature).

10. This general problem is associated with the particular problem of creating a superhard substance, about as hard as or even harder than diamond. On the basis of the effect of chemical composition on the properties of a simple substance, it is possible in principle to solve the problem of increasing the hardness of the hardest substance – the modification of carbon known as diamond. This can be attained by the synthesis of a series of compounds of carbon with metals – carbides and solid solutions of elements in carbon with preservation of diamondlike structures – and by increasing the strengths of the bonds between atoms entering into the composition of such compounds and solid solutions of carbon. In this connection we must point out the important task of investigating the interaction of such nonmetals as carbon and boron with metals from the point of view of the formation of solid solutions of metals in these nonmetals and of refractory compounds in which the nonmetals predominate. It is desirable, for example, to verify Baikov's views on the possible existence of solid solutions of iron in carbon [50].

The tasks that we have enumerated – and the list is far from complete – are of great theoretical and practical importance for metallochemistry. There are grounds for believing that unified efforts in these directions will result in considerable progess in the theory and the development of new metallic materials: alloys that are stable and of high mechanical strength at high temperatures, magnetic and nonmagnetic alloys, and conducting and semiconducting materials, which are so necessary for rapidly developing modern technology.

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RADIOCHEMICAL INVESTIGATION OF HIGH-ENERGY SPALLATION REACTIONS RESULTING FROM THE BOMBARDMENT OF SEPARATED COPPER ISOTOPES WITH 660-Mev PROTONS

A. N. Murin and I. A. Yutlandov

High-energy spallation reactions due to the bombardment of elements of the middle part of Mendeleev's system with fast particles have been examined in numerous radiochemical investigations: V [1 – 3], Mn [1], Fe [4], Co [1, 5 – 8], Cu [9 – 21], Zn [22], As [23]. A particularly careful study has been made of copper in the form of the natural mixture of isotopes (Cu^{63} – 69.1%, Cu^{65} – 30.9%). We have studied the high-energy spallation reactions resulting from the bombardment of separated copper isotopes with 660-Mev protons in the synchrocyclotron of the Unified Institute of Nuclear Investigations.

EXPERIMENTAL

Chemical Isolation of the Reaction Products. The targets were plates of pure copper (in the case of natural copper) or copper powder wrapped in aluminum foil (in the case of the separated isotopes).* After being bombarded, the target was dissolved in nitric acid. Nitric acid was replaced by hydrochloric acid by evaporation with concentrated hydrochloric acid. As it was necessary to carry out repeated bombardments of the separated copper isotopes, they were recovered, and were then obtained in the form of $Cu^{63}O$ and $Cu^{65}O$. Targets made from the oxides of the separated copper isotopes were dissolved directly in hydrochloric acid.

We shall now outline the methods of isolating fractions of various elements in the radiochemically pure form. Many of the operations were repeated many times.

Cu. Precipitation of CuS from 2 N HCl with H_2S. Dissolution of CuS and precipitation of hydroxides insoluble in ammonia from the resulting solution on a precipitate of $Fe(OH)_3$. Reduction of Cu^{2+} to Cu^{+} with SO_2, and precipitation of CuCNS.

Ni. Separation of ammonia-insoluble hydroxides with $Fe(OH)_3$. Precipitation of Ni with dimethylglyoxime in dilute acetic acid.

Fe. Extraction with diethyl ether from 6 N HCl. Precipitation of ferric hydroxide with excess of ammonia.

Mn. Precipitation of MnO_2 from solution in concentrated nitric acid with the aid of $KClO_3$.

Cr. Oxidation of Cr^{3+} to CrO_4^{2-} with the aid of $KClO_3$ in nitric acid solution. Precipitation of $BaCrO_4$.

Co. After removal of Mn, Cr, and Ba, precipitation of CoS with $(NH_4)_2S$. Dissolution of CoS. Precipitation of ammonia-insoluble hydroxides from the resulting solution together with $Fe(OH)_3$. Precipitation of Co from acetic acid solution with 1-nitroso-2-naphthol. In some cases, in order to speed up the isolation process, Co was precipitated in the form of potassium hexanitrocobaltate.

Ca. Separation of sulfides of elements of the third analytical group. Precipitation of Ca as oxalate.

K. Separation of elements of the second analytical group as oxalates (with Ca oxalate). Precipitation of K with perchloric acid in butyl alcohol.

* The preparations at out disposal had the following compositions: 1) Cu^{63}: 93.2% Cu^{63}, 6.8% Cu^{65}, 0.06% Fe; 2) Cu^{65}: 93.7% Cu^{65}, 6.3% Cu^{63}, 0.06% Fe.

Sc. Separation of Sc, Ti, and Fe hydroxides with ammonia. Precipitation of Sc as fluoride.

P. Precipitation of P as ammonium phosphomolybdate. Dissolution of the precipitate in ammonia in presence of Ti, V, and citric acid, and precipitation of ammonium magnesium phosphate with magnesia mixture.

In all the cases indicated we determined the chemical yield of the isotope carriers that we used.

Method of Counting and Determination of Yields. The activities of the preparations isolated were determined in the usual way with a standard end-window counter TM-20 [24]. For the count of X-ray quanta emitted by radioactive isotopes as a result of electron capture, we made use of beryllium filters, which completely absorb corpuscular and X-ray (L-rays) radiation. The efficiency of the count of X-ray K quanta was determined by comparison of rates of count of open and filtered preparations of radioactive isotopes undergoing both β^+-decay and E-capture (the contributions to decay of the two possible routes were known from the literature [25]). In the case of the Co fraction, the long-lived component of which contains Co^{56} * and Co^{58} with almost equal half-lives (T = 72 days), the resolution of the gross decay curve into the individual components is impossible. Hence, the cobalt preparation was measured not only in the open form, but also with an aluminum filter (150 mg/sq.cm) which absorbed the relatively soft β^+-radiation of Co^{58} (E_{max} = 0.47 Mev). The yield of Co^{58} was determined from the difference in the counts.

TABLE

Isotope	Yield (millibarns)			σ (natural Cu) calculated from σ (Cu^{65}) and σ (Cu^{63})
	σ (natural Cu)	σ (Cu^{65})	σ (Cu^{63})	
Cu^{64}	9.7	31.4	0.36	—
Ni^{57}	0.85	0.38	0.78	0.66
Co^{61}	—	4.8	—	—
Co^{58}	14.0	15.2	14.1	14.4
Co^{56}	8.3	7.8	9.6	9.0
Co^{55}	—	1.14	—	—
Fe^{59}	0.56	1.54	0.25	0.65
Fe^{55}	14.3	18.5	12.4	14.3
Mn^{54}	18.0	23.6	20.4	21.4
Mn^{52}	16.3	14.6	16.1	15.6
Cr^{51}	17.7	11.7	12.6	12.3
Sc^{47}	—	—	2.2	—
Sc^{46}	5.1	4.9	2.6	3.3
Ca^{47}	0.038	0.063	0.017	0.031
Ca^{45}	0.90	1.05	0.48	0.66
K^{43}	—	—	0.40	—
K^{42}	—	—	0.84	—
P^{32}	0.67	0.72	0.79	0.77

In all experiments the reference nuclide Ca^{45} was isolated and its activity was determined. Absolute cross sections for the formation of individual nuclides from natural copper were determined by comparison of the yield of Ca^{45} with that of Na^{24} in the reaction Al^{27} (p, 3pn)Na^{24}, the cross section of which is accepted as being 11 millibarns [24]. In the case of separated isotopes, this determination was rendered difficult by the practical impossibility of attaining the correct mutual disposition of the monitor aluminum foils and the copper powder. For Cu^{65}, therefore, the cross sections for the formation of nuclides were determined by comparison with the yield of Cu^{64} **, the cross section for which was determined in experiments with ordinary copper. The cross sections for the formation of individual nuclides from Cu^{63} were determined as differences from the corresponding cross sections for formation from natural copper and Cu^{65}:

$$\sigma(Cu^{63}) = \frac{\sigma\,(Cu) - 0.309\,\sigma(Cu^{65})}{0.691}.$$

* The scheme of the decay of Co was given in [26].

** It was shown that the yield of the reaction C^{63} (p, π^+) Cu^{64} can be neglected in comparison with that of the reaction Cu^{65} (p, pn) Cu^{64}.

In this case relative yields were determined also by direct isolation of the products from Cu^{63}. The values obtained were normalized so that the sum of the squares of the differences between the directly measured values and those calculated by the above equation was as small as possible. The final results of our experiments are given in the table.*

The possible error in the determination of cross sections [not including possible error associated with the determination of the cross section for the reaction Al^{27} (p, 3 pn)Na^{24}] is about 30%, except in the case of isotopes undergoing pure E-capture (Fe^{55}, Mn^{54}, Cr^{51}), for which it may attain 50%.

DISCUSSION OF RESULTS

Values of cross sections for the formation of nuclides of a given isotopic number $I = N - Z = A - 2Z$ fit to smooth curves such as that shown in Fig. 1. As will be seen from Fig. 1, it is possible to bring curves for Cu^{63} and Cu^{65} into coincidence by a displacement of the axis of abscissae so that at each point the numbers of protons and neutrons lost are the same for Cu^{63} as for Cu^{65}. Some nuclei of high atomic number form exceptions (Fig. 2). If we exclude such cases ("fine structure" of the yields surface – Fig. 3), we can construct a universal yields surface in the system of coordinates $A_T - A_{NP}$, $I_T - I_{NP}$, and log σ, which is applicable to $_{29}Cu^{63}$, to $_{29}Cu^{65}$, and apparently also to some other nuclei for which Z and A have values close to those of copper, e.g. $_{27}Co^{59}$ (the subscripts T and NP refer to target and nuclear product, respectively)**. The small cross section for the formation of Ca^{47} (Fig. 2) is possibly determined by the low density of energy levels of the doubly "magic" intermediate nucleus Ca^{48} ($Ca^{48} \rightarrow Ca^{47} + n$).

For the calculation of the yields of stable nuclides and of radioactive nuclides having half-lives of inconvenient magnitude, Rudstam [28] proposed a semiempirical equation of the form:

$$\sigma(A_i, Z_i) = \exp[PA_i - Q - R(Z_i - SA_i)^2], \quad (1)$$

in which $\sigma(A_i, Z_i)$ is the cross section for the formation of the given nuclear product and P, Q, R, and S are constant parameters determined so as to give the best agreement between calculated and directly measured values of $\sigma(A_i, Z_i)$. According to our calculations, the values of P, Q, R, and S are practically the same for Cu^{63} and Cu^{65} (for E_p = 660 Mev) and can be assumed to have the values P = 0.15, Q = 5.1, R ≈ 1.6, and S = 0.467. The calculated values of $\sigma(A_i, Z_i)$ then agree with the measured values accurately within a factor of 2***. An exception is found in the case of the formation of Ni^{57} from Cu^{65}, for which there is a substantial discrepancy between measured ($\sigma = 0.38 \cdot 10^{-27}$ sq.cm) and calculated ($\sigma = 1.95 \cdot 10^{-27}$ sq.cm) values of σ. It must be pointed out that a study has been made [8] of excitation functions for some individual reactions occurring in the bombardment of cobalt with 100 Mev protons. The low yields of $_{28}Ni^{57}$ and $_{28}Ni^{56}$ are explained as a purely shell effect (Z = 28). However, in the case of Cu^{63} the yield of Ni^{57} is close to the calculated value ($\sigma_{expt} = 0.78 \cdot 10^{-27}$ sq.cm; $\sigma_{calc} = 0.62 \cdot 10^{-27}$ sq.cm). It follows that a low value of σ (Ni^{57} from Cu^{65}) is probably determined simply by the correlation between the numbers of protons and neutrons lost by the target nucleus.

The parameter P in Equation 1 is a measure of the slope of the curve for the relation between the logarithm of the sum of yields of nuclei of given mass number and A. The values of P**** (for copper) for bombarding protons of different energies are shown in Fig. 4, in which the point corresponding to the case we have studied is indicated by an arrow.

The authors consider it to be their pleasant duty to express their deep gratitude to M. G. Meshcheryakov, V. P. Dzhelepov, and the operating staff of the synchrocyclotron of the Unified Institute of Nuclear Investigations for cooperation in the performance of this work.

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* Some preliminary data are given in one of our papers [27].

** We must point out the possibility of the effect of the evenness or oddness of the numbers of protons and neutrons in the target nucleus.

*** The details of our calculations are given in a thesis by one of the authors [29].

**** Values of P taken from the paper [28].

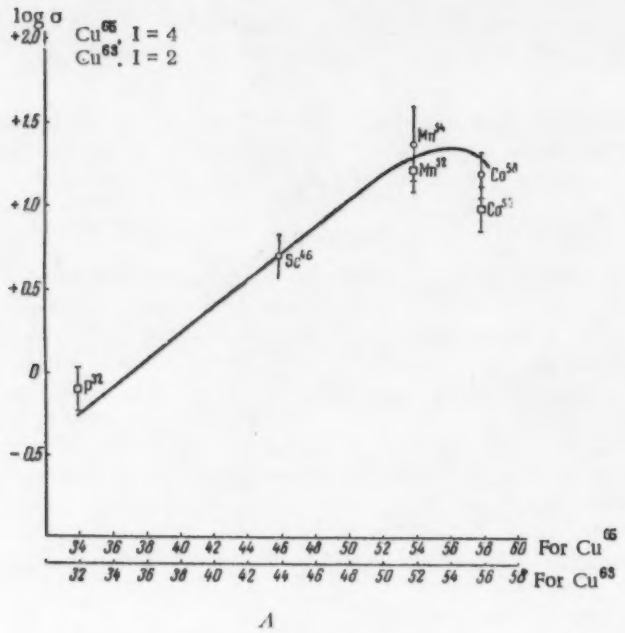
log σ
+2.0
+1.5
+1.0
+0.5
0
-0.5
Cu65, I = 4
Cu63, I = 2
Mn54
Mn52
Co56
Co57
Sc46
P32
34 36 38 40 42 44 46 48 50 52 54 56 58 60 For Cu65
32 34 36 38 40 42 44 46 48 50 52 54 56 58 For Cu63
A

Fig. 1.

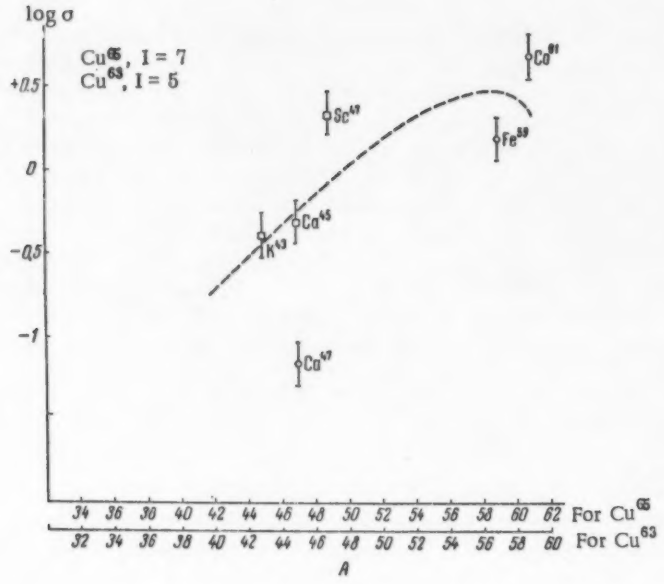
log σ
+0.5
0
-0.5
-1
Cu65, I = 7
Cu63, I = 5
Co61
Sc47
Fe59
Ca45
K43
Cu47
34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 For Cu65
32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 For Cu63
A

Fig. 2.

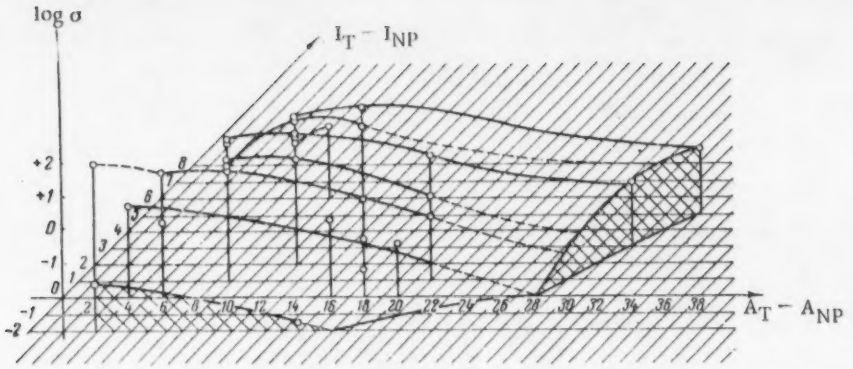

Fig. 3.

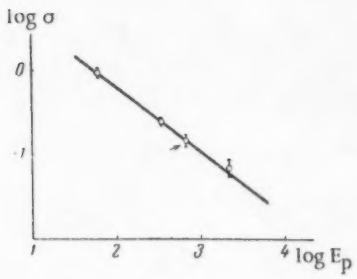

Fig. 4.

SUMMARY

1. Separated copper isotopes were bombarded with 660-Mev protons and the yields of some of the radioactive spallation products were determined.

2. A universal surface representing yields of nuclear products was constructed. The small cross section for the formation of Ca^{47} may be explained by the completion of nucleon shells in the intermediate nucleus $_{20}Ca^{48}$.

3. Cross sections for the formation of nuclear products are given quite satisfactorily by the equation:

$$\sigma(A_i, Z_i) = \exp[0{,}15A_i - 5.1 - 1.6(Z_i - 0.467A_i)^2].$$

The cross section for the formation of Ni^{57} from Cu^{65} cannot be expressed by this equation, and we consider that this is to be explained by a correlation effect.

4. The value that we obtained for the parameter P (about 0.15) lies on the straight line for log P against log E_p constructed for bombarding protons ranging in energy from 60 to 2200 Mev.

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* [See C. B. translation].

ADSORPTION OF SURFACE-ACTIVE SUBSTANCES ON AN IRON ELECTRODE IN AN ALKALINE SOLUTION

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In order to elucidate the mechanisms whereby various additions affect electrode processes it is desirable to study the adsorption of the additives on the electrodes as well as carry out kinetic measurements. In many cases a convenient method of measuring adsorption is afforded by measurements of the capacity of the electrode in an alternating current. Thus, adsorption of organic compounds is generally accompanied by reduction in the capacity of the electrode in a certain range of potentials in the vicinity of the potential of zero charge, and also by the appearance of characteristic capacity maxima ("desorption peaks") at the limits of this potential range [1]. Considerable practical interest is presented by the selection of surface-active substances that can affect the kinetics of electrode processes at an iron electrode in alkaline solutions; in particular, it is of great importance to find additives that will raise the hydrogen overvoltage at an iron electrode and so reduce the autosolution of this electrode in an alkali accumulator.

EXPERIMENTAL

We studied the relation between the capacity of an iron electrode and its potential in 2 N NaOH for potentials ranging from − 0.5 to + 1.5 v (against a hydrogen electrode in the same solution) in presence of additives, namely, tetrabutylammonium sulfate, 2-naphthalenesulfonic acid, hexanoic acid, octyl alcohol, sodium arsenite, tannin, alizarin, and phenol. Simultaneously with measurements of capacity, hydrogen-overvoltage curves were determined.

The electrode investigated was a fine wire (diameter 0.22 mm) of chemically pure iron placed coaxially in a platinum cylinder, which served as an accessory electrode for the passage of alternating current. All solutions were prepared by dissolving chemically pure reagents in doubly distilled water, and before the experiments they were saturated with nitrogen carefully purified from oxygen. The capacity of the electrode in an alternating current was measured with an impedance-compensation system with separate compensation for capacity and ohmic components. The alternating current used for the measurements had a frequency of 5000 cycles per second. Under these conditions the most probable equivalent scheme of the electrode is a capacity and resistance connected in parallel, and therefore, after subtracting the resistance of the solution, we generally recalculated the measured values of capacity (C_1) and resistance (R_1), corresponding to capacity and resistance in series, to give the value C_2, corresponding to connection in parallel. In most cases the values of C_2 differed little from the corresponding values of C_1, since the value of the tangent of the phase shift was usually greater than unity.

At the beginning of the experiment the iron electrode was subjected to cathodic polarization with a current of high density ($5 \cdot 10^{-2}$ amp/sq. cm).* After this preparation capacity-potential curves were determined first with cathodic and then with anodic polarization.

The relation between the capacity of the electrode (C_2) and the potential in pure 2 N NaOH at 5000 cycles per second is represented in Fig. 1. As the potential of the electrode is displaced in the positive direction, there is a gradual fall in capacity, probably due to increase in the thickness of the passivating oxide layer on

* The stationary potential of such a semipassive electrode was 0.1-0.2 v against a hydrogen electrode in the same solution.

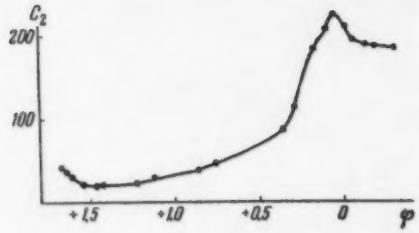

Fig. 1. Relation between capacity and potential of electrode in 2 N NaOH.

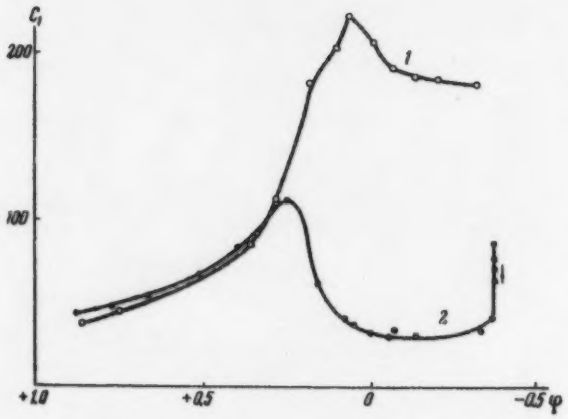

Fig. 2. Effect of tannin on the capacity of the electrode; 1) 2 N NaOH; 2) 2 N NaOH + 2% tannin

the iron surface. In the presence of additions of tetrabutylammonium sulfate and naphthalenesulfonic acid there was a slight lowering of capacity (by 10-20%) at potentials more negative than 0.3 v. In presence of additions of hexanoic acid and octyl alcohol no lowering of capacity was observed. These additions have almost no effect on the value of the hydrogen overvoltage; a small lowering of the hydrogen overvoltage (30-40 mv) is observed only in the case of hexanoic acid.

These results show that, within the limits of accuracy of our experiments, we were unable to detect the absorption of these organic substances on an iron surface in an alkaline solution. The reason for the feeble adsorbability of these typical surface-active additives probably lies in the fact that an iron surface in an alkaline solution is almost always oxidized to a greater or lesser extent. Evidence of the presence of an oxidized surface on the iron in our experiments is to be found, in particular, in the high value of the slope of the overvoltage curve (0.2 v). According to the results of Rozentsveig and Kabanov [2], in the case of an unoxidized iron surface the slope is 0.1 v, whereas in the case of oxidized iron it rises to 0.2 v. The literature [3] indicates that oxidized iron has a considerably lower tendency to adsorb organic substances than an iron surface free from oxides. It is probable that the presence of oxides on the metal surface results in such powerful hydrophilization of the surface that specific adsorption becomes impossible. At the same time, adsorption due to chemical interaction between the particles being adsorbed and the electrode surface can occur also at an oxidized surface. Since the typical surface-active additives that we tried had practically no effect on the capacity of an oxidized iron surface, it would appear that, under the given conditions, chemical adsorption also did not occur.

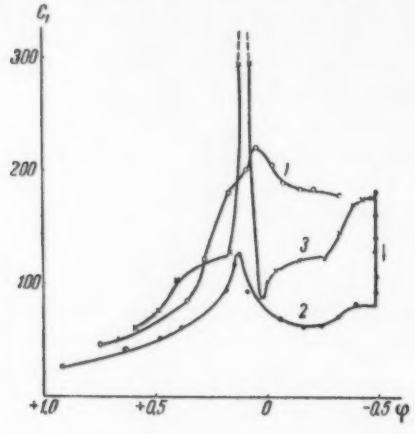

Fig. 3. Effects of alizarin and phenol on the capacity of the electrode: 1) 2 N NaOH; 2) 2 N NaOH + 0.3% alizarin; 3) 2 N NaOH + 0.7 N C_6H_5OH

As pointed out previously [4], it is of interest to study the effect of additions of compounds that readily react chemically with iron, both in the ionic form and in the form of hydroxides, and so should be adsorbed on an oxidized iron surface. As additives of this kind we selected tannin, alizarin, phenol, and arsenious oxide. In presence of 2% tannin, the capacity of an iron electrode (C_1) in the negative potential region (from − 0.3 to 0.0 v) is reduced to approximately one-sixth of the capacity in pure sodium hydroxide solution (Fig. 2). At higher tannin concentrations (6.5%) there is no further lowering of capacity. At potentials more positive than 0.4 v, additions of tannin have no effect on capacity, and at potentials of 0.9-1.0 v, judging from the character of the dependence of potential on current density and on rate of stirring of the solution, anodic oxidation of the tannin occurs. An analogous effect on the

capacity of an iron electrode is shown also by alizarin and by phenol. As can be seen from Fig. 3, addition of 0.3% of alizarin results in a reduction of the electrode capacity to one-third at potentials ranging from − 0.5 to 0.0 v. Addition of phenol also results in an appreciable reduction in capacity at negative potentials. The sharp drop in the capacity of an iron electrode observed on the introduction of tannin, alizarin, or phenol into the alkaline solution indicates that these substances are adsorbed on the iron surface*. Moreover, at high concentrations of phenol (which, unlike the other additives, is of high solubility in alkali), the capacity-potential curve has a high maximum, which appears to be a desorption peak** [1, 5]; this again indicates adsorption of phenol at negative potentials. As can be seen from Figures 2 and 3, at more positive potentials the effects of tannin, alizarin, and phenol on the capacity of the electrode almost disappear, which indicates that they are desorbed from the electrode surface.

The effect of additions of tannin, alizarin, and phenol on hydrogen overvoltage is shown in Fig. 4. According to Levina's results [4], which refer to the rise in the hydrogen overvoltage at an iron powder electrode at high current density ($5 \cdot 10^{-3} - 5 \cdot 10^{-2}$ amp/sq.cm), in presence of tannin the rise is 40-60 mv and in presence of alizarin it is 60-80 mv.*** It must be pointed out that, when the electrode is immersed in a solution having additions of tannin and alizarin under a powerful cathodic current, constant values of overvoltage and capacity are not established immediately: these is a slow rise in overvoltage with simultaneous gradual lowering of capacity (Figures 2 and 3), and the overvoltage attains a constant value in 20-30 minutes simultaneously with cessation of change in capacity. This shows that raising of the overvoltage by tannin and alizarin is due to the chemical adsorption of these substances. In presence of additions of phenol no rise in overvoltage is observed.

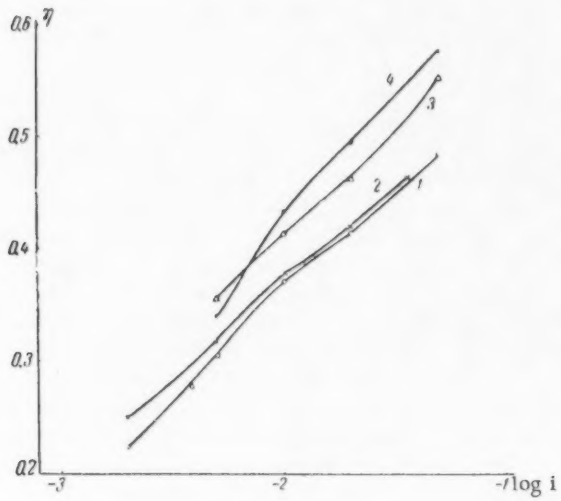

Fig. 4. Effects of tannin, alizarin, and phenol on hydrogen overvoltage: 1) 2 N NaOH; 2) 2 N NaOH + + 0.7 N C_6H_5OH; 3) 2 N NaOH + 2% tannin; 4) 2 N NaOH + 0.3% alizarin.

As well as the effects of the addition of organic substances on the capacity of the iron electrode in alkaline solutions, we studied also the effect of additions of arsenious oxide. Figure 5 shows the relation between the capacity of the electrode (C_2) and its potential for 2 N NaOH with additions of 0.002 and 0.2 M $NaAsO_2$ (arsenic was introduced into the solution as As_2O_3). At the most negative cathodic potentials (from − 0.5 to − 0.6 v), the capacity of the electrode in solutions containing the additions was 100-110 microfarads/sq.cm, and it remained almost unchanged with prolonged cathodic polarization. When the cathode current density was reduced to 2-5 x 10^{-3} amp/sq.cm (the electrode potential then shifted to a value of from − 0.40 to − 0.45 v) in the solution with an addition of 0.2 M $NaAsO_2$, there was a slow fall in capacity down to very low values of the order of 10 microfarads/sq.cm and these values of capacity were maintained over a wide range of potentials. On the capacity-potential curve based on determinations made in the direction from positive potentials to negative (after the electrode had been subjected to powerful anodic polarization), a high

* We give results of measurements of the capacity of electrodes in presence of additions of tannin, alizarin, and phenol for an equivalent scheme of series connection of capacity and resistance, because the phase shift is appreciably greater than 45° in these cases, so that the values of capacities corresponding to the series scheme (C_1) differ little from the values corresponding to the parallel scheme (C_2).

** This maximum is observed for cathodic polarization and is therefore not associated with the anodic oxidation of phenol.

*** These effects of raising the overvoltage are observed when alkaline solutions containing the additives are prepared several days before the beginning of the experiment (tannin) or when polarization experiments have already been carried out in the given solution (alizarin); in the case of freshly prepared solutions effects of enhanced overvoltage are insignificant (less than 40 mv). It would appear that products formed in the slow processes of polymerization or oxidation of the additives in alkaline solutions can have a great effect on overvoltage.

maximum is observed (Fig. 5, Curve 3') in approximately the same range of potentials as on the capacity curve obtained in absence of arsenic.

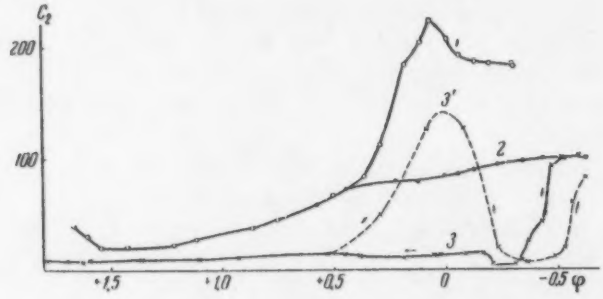

Fig. 5. Effect of $NaAsO_2$ on the capacity of the electrode; 1) 2 N NaOH; 2) 2 N NaOH + 0.002 M $NaAsO_2$; 3) and 3') 2 N NaOH + 0.2 M $NaAsO_2$.

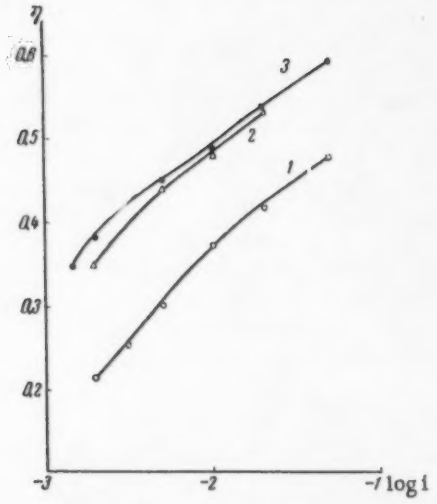

Fig. 6. Effect of $NaAsO_2$ on hydrogen overvoltage: 1) 2 N NaOH; 2) 2 N NaOH + 0.002 M $NaAsO_2$; 3) 2N NaOH + 0.2 M $NaAsO_2$.

This maximum probably indicates partial desorption of arsenic from the strongly oxidized surface of the iron electrode. In fact, the sharp fall in capacity after the maximum on Curve 3' is observed only for cathodic polarization when potentials ranging from − 0.1 to − 0.2 v are attained, i.e. adsorption of arsenic occurs only after partial reduction of the surface oxides. In solutions to which only a small amount of arsenic (0.002 M) has been added, no sharp fall in capacity is observed, although the capacity in the potential range of − 0.3 to + 0.2 v is still reduced to almost one-half of its value in pure sodium hydroxide solution. Figure 6 gives hydrogen-overvoltage curves for solutions with the same additions of arsenic. It will be seen that addition of very small amounts of $NaAsO_2$ (0.002 M) raises the hydrogen overvoltage by about 100 mv and further increase in the concentration of arsenic has almost no effect on the overvoltage. We must mention that, at potentials corresponding to powerful cathodic polarization, evolution of hydrogen at the electrode is accompanied by partial reduction of AsO_2^- ions to As.

The question naturally arises of whether the above-described raising of hydrogen overvoltage and reduction in the capacity of the electrode is not associated with the appearance of a surface layer of reduced arsenic covering much of the iron surface and whether the measured values of capacity and overvoltage are not really to be attributed to the arsenic, rather than to the iron electrode. It is difficult to solve this question finally on the basis of our results. However, the fact that, even with prolonged cathodic polarization at a high current density at potentials ranging from − 0.5 to − 0.6 v, the capacity of the electrode is not reduced, whereas at somewhat higher potentials the capacity falls to approximately one-tenth of its original value, indicates that this reduction in capacity is due mainly not to the formation of a layer of reduced arsenic, but to some other effect, e.g. the formation of an adsorptional surface compound of arsenic with iron oxides. Thus, according to the literature [6], hydrated ferric oxide is capable of absorbing arsenious oxide from solution and the process has the character of reversible adsorption.

DISCUSSION OF RESULTS

This investigation has shown that additions of various typical ionic and nonionic surface-active compounds (tetrabutylammonium sulfate, naphthalenesulfonic acid, hexanoic acid, octyl alcohol) have little effect on the hydrogen overvoltage at an iron electrode in alkaline solutions and do not reduce the capacity of the electrode appreciably; these substances are apparently not adsorbed on an iron surface under the given conditions. On the other hand, additions of substances such as tannin, alizarin, phenol, and arsenious oxide raise the hydrogen overvoltage somewhat (except in the case of phenol) and greatly reduce the capacity of the iron electrode at negative potentials (from + 0.1 to − 0.4 v); at more positive potentials these additions (apart from arsenic) have almost no effect on the capacity of the electrode. Hence, these additions are adsorbed strongly at negative potentials and are desorbed at more positive potentials. The common characteristic determining the chemical properties of the organic additives (tannin, alizarin, and phenol) is the presence of hydroxy groups of the phenolic type. In alkaline solutions these compounds dissociate to a greater or lesser extent with formation of the corresponding anions. Numerous data in the literature [7] show that these compounds readily react in the form of the ion with hydrated metal oxides, and in particular iron oxides, with formation of insoluble adsorption compounds. For example, in the interaction of alizarin with hydrated ferric oxide it may be supposed that the process proceeds as follows:

$$Fe(OH)_3 + NaAz \rightarrow Fe\begin{matrix}\diagup OH \\ \diagdown Az\end{matrix} + NaOH.$$

The resulting molecule of the alizarin compound of iron appears to remain attached to the surface oxide, i.e. a new phase compound is not formed, but an adsorption compound is produced. It is known [8], moreover, that the surface of a smooth iron electrode in an alkaline solution is always more or less oxidized; under these conditions even prolonged cathodic polarization at high current density will not succeed in reducing the iron surface completely. It is therefore very probable that the mechanism of the adsorption of tannin, alizarin, and phenol at an iron electrode also consists in the chemical interaction of the hydroxy groups of these compounds or the corresponding anions with surface oxides of the iron.

We express our indebtedness to S. D. Levina for valuable advice, which was of great help to us in carrying out this work.

SUMMARY

1. The effects of various surface-active additives on the electrochemical behavior of an iron electrode in 2 N NaOH were investigated with the aid of measurements of capacity in an alternating current and of determinations of polarization curves.

2. Octyl alcohol molecules and tetrabutylammonium, naphthalenesulfonate, and hexanoate ions do not reduce the capacity of an iron electrode and have little effect on the hydrogen overvoltage; these species, therefore, are not adsorbed appreciably on the iron surface.

3. Compounds that are able to react chemically with ions or oxides of iron (tannin, alizarin, arsenious oxide, and to a lesser extent phenol) greatly reduce the capacity of an iron electrode at potentials more negative than the stationary potential, and they also raise the hydrogen overvoltage to some extent; this indicates that these compounds are adsorbed at the slightly oxidized iron surface. At potentials that are more positive than the stationary potential, these additives (with the exception of arsenic) have no effect on the capacity and are probably desorbed from the iron surface.

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* [See C. B. translation].

RELATION BETWEEN THE CATALYTIC ACTIVITY OF BINARY COMPOUNDS OF GROUP II METALS WITH NONMETALS AND THE POSITIONS OF THE ELEMENTS IN MENDELEEV'S PERIODIC SYSTEM

COMMUNICATION 2: CATALYTIC DECOMPOSITION OF ISOPRYOPYL ALCOHOL OVER OXIDES OF GROUP IIB METALS

O. V. Krylov, S. Z. Roginsky, and E. A. Fokina

The catalytic properties of oxides of Group IIB metals have been studied much more thoroughly than the properties of alkaline-earth oxides. Sabatier [1], in a study of the decomposition of alcohols, placed MgO, ZnO, and CdO among the typical dehydrogenation catalysts. According to his results, BeO brings about simultaneous dehydrogenation and dehydration of alcohols. Later work [2, 3] showed that such a "typical" dehydrogenation catalyst as zinc oxide can bring about dehydration. The investigations of Zhabrova, Kutseva, and Roginsky [4, 5] show that the dehydrating properties of ZnO observed by some workers are probably to be attributed to the presence of impurities of an acidic character entrained by the catalyst during its preparation: pure zinc oxide, carefully washed free from impurities, decomposes isopropyl alcohol by dehydrogenation.

Similar difficulties are found when we compare the data of various investigators on other oxides. Different authors used different raw materials and different procedures in the preparation of catalysts, the catalytic reaction was studied at different temperatures, and different methods of investigation were used. Hence, for comparison of the catalytic activities of various oxides, and particularly for comparison with the results of our investigation of alkaline-earth oxides [6], it was desirable to reinvestigate the catalytic decomposition of isopropyl alcohol over oxides of Group IIB metals, which had been studied previously by other investigators. The present paper is devoted to an account of this investigation. Particular attention was given to the comparative catalytic activities of preparations of a given oxide obtained by different methods.

EXPERIMENTAL

The following catalysts were used for the decomposition of isopryopyl alcohol.

Beryllium oxide BeO prepared 1) by decomposition of $BeCO_3$ at 650° for two hours; 2) by precipitation of $Be(OH)_2$ from $BeSO_4$ solution with sodium hydroxide and calcination of the hydroxide at 450° for two hours; 3) by precipitation of $Be(OH)_2$ from $BeCl_2$ solution with sodium hydroxide and calcination of the hydroxide at 450° for two hours; 4) by decomposition of $Be(NO_3)_2$ at 650° for two hours.

Magnesium oxide MgO prepared 1) by decomposition of $MgCO_3$ at 450° for four hours; 2) by precipitation of $Mg(OH)_2$ from $Mg(NO_3)_2$ solution with sodium hydroxide and calcination of the hydroxide at 450° for two hours; 3) by precipitation of $Mg(OH)_2$ from $MgSO_4$ solution with sodium hydroxide and calcination of the hydroxide at 450° for two hours.

Zinc oxide ZnO prepared 1) by precipitation of $Zn(OH)_2$ from $Zn(NO_3)_2$ solution with sodium hydroxide and calcination of the hydroxide at 450° for three hours; 2) by precipitation of $Zn(OH)_2$ from $ZnSO_4$ solution with sodium hydroxide and calcination of the hydroxide at 450° for four hours; 3) by precipitation of $Zn(OH)_2$ from $ZnSO_4$ solution [possibly $ZnCl_2$ is intended here – Publisher] with sodium hydroxide and calcination of

the hydroxide at 450° for four hours.

Cadmium oxide CdO prepared 1) by precipitation of Cd $(OH)_2$ from Cd $(NO_3)_2$ solution with sodium hydroxide and calcination of the hydroxide at 450° for four hours; 2) by precipitation of Cd $(OH)_2$ from $CdCl_2$ solution with sodium hydroxide and calcination of the hydroxide at 450° for two hours; 3) by precipitation of Cd $(OH)_2$ from $CdCl_2$ solution [$CdSO_4$ is probably intended here – Publisher] and calcination of the hydroxide at 450° for two hours; 5) [Presumably 4) is intended – Publisher] decomposition of Cd $(CO_3)_2$ at 450° for two hours.

Oxides prepared by decomposition of carbonates and nitrates had a smaller surface than oxides obtained by precipitation and decomposition of hydroxides. It is possible that in certain cases (BeO) this is due to the fact that the decomposition of carbonates and nitrates was carried out at a higher temperature (650°) than in the case of hydroxides (450°).

In the precipitation of hydroxides tests were made for anions in the wash waters (washing was continued until the tests were negative). A somewhat more detailed study was made of the retention and removal of anions in the case of sulfate retention by beryllium and cadmium hydroxides. For this purpose some Na_2SO_4 labeled with radiosulfur S^{35} was added to the original $BeSO_4$ and $CdSO_4$ solutions before precipitation of the hydroxides Be $(OH)_2$ and Cd $(OH)_2$ with sodium hydroxide. Washing was effected with hot distilled water. The sulfate content of the catalyst during washing was determined by radiochemical analysis.

In this way we prepared samples of BeO having Na_2SO_4 contents of 2.04, 0.55, 0.32, and 0.28 % by weight and samples of CdO having Na_2SO_4 contents of 0.23, 0.19, 0.12, and 0.63% by weight.

The procedure employed in the study of the decomposition of isopropyl alcohol under flow conditions was similar to that already described [6]. The effects of complications due to diffusion conditions were checked by examining the influence of granule size of the catalyst on the rate of gas liberation and the composition of the products for some samples of BeO, MgO, ZnO, and CdO. In most cases increase in granule diameter from 2-5 to 8-10 mm had no effect. Thus, for CdO obtained by precipitation of the hydroxide by sodium hydroxide from $CdSO_4$ solution and subsequent decomposition at 450°, with granules of diameter 2-3 mm the rate of gas liberation for an alcohol feed of 0.25 ml/minute and a temperature of 240° was 36 ml per minute per gram of catalyst and with granules of diameter 8 mm under the same conditions the rate of gas liberation was 29 ml per minute per minute per gram; the corresponding figures for 280° were 124 and 140, for 300° 200 and 208, and for 330° 237 and 250 ml per minute per gram. The content of unsaturated hydrocarbons in the gas was also substantially unchanged. Only for a few individual catalysts were diffusion complications found. Thus, for ZnO obtained by precipitation of the hydroxide by sodium hydroxide from $Zn(NO_3)_2$ solution and subsequent decomposition at 450°, with increase in granule diameter from 2 to 8 mm gas liberation at 300° (alcohol feed 0.30 ml/minute) was reduced by 26%, the corresponding figures for 350° and 400° being 30% and 35% respectively.

Some experiments were carried out also on the decomposition of isopropyl alcohol in the adsorbed layer on ZnO. In this case the procedure was similar to that described by Levin [7]. The surface area of the catalysts was determined with the aid of a McBain balance applied to the adsorption of heptane, the calculation being done by the BET method.

EXPERIMENTAL RESULTS

Table 1 gives the results of experiments on the catalytic decomposition of isopropyl alcohol over beryllium oxide obtained by various methods – both pure and with additions of Na_2SO_4. The figures given in Table 1 correspond to the stationary state (see previous paper [6]).

Figure 1 gives curves for the relation between the logarithm of the rate of liberation of hydrogen and the reciprocal of the temperature, and Fig. 2 gives curves for the relation between the logarithm of the rate of liberation of propene and 1/T. From these graphs we calculated approximate activation energies, which are given in Table 1. For some samples we studied the relation between the rate of gas liberation and the time of contact (rate of alcohol feed). Figure 3 gives kinetic curves for the relation between the rate of liberation of hydrogen over beryllium oxide and the rate of the alcohol feed, and Fig. 4 gives the same relation for zinc oxide prepared by precipitation of the hydroxide from a solution of the nitrate with sodium hydroxide and subsequent thermal decomposition. It will be seen from these graphs that for low and medium

TABLE 1

Experimental Results on the Decomposition of Isopropyl Alcohol over Beryllium Oxide.

Catalyst	Specific surface (sq.m/g)	Temperature (°C)	Rate of gas liberation (ml per ml of alcohol per minute)	Propene content of gas (%)	Act. energy for dehydrog. E_{H_2} (cal/mole)	Act. energy for dehydrat. E_{H_2O} (cal/mole)	Selectivity coefficient $\frac{[H_2]}{[C_3H_6]}$
BeO from carbonate	54	356	5.8	27	29 000	35 000	2.7
		376	20	41			1.44
		406	67	46			1.17
		434	172	60			0.67
BeO from nitrate	43	360	10.4	30	21 000	35 000	2.3
		406	53	47.5			1.11
		432	79	59			0.69
		454	179	69.5			0.44
BeO from nitrate via hydroxide	108	312	5.5	9.0	25 000	36 000	10.1
		382	68	9.5			9.5
		404	110	10.5			8.5
		446	200	13			6.7
BeO from chloride via hydroxide	93	336	12.5	7.1	27 000	32 000	13.1
		356	98	8.4			10.9
		382	161	9.9			9.1
		426	320	11.5			7.7
BeO with addition 0.28% Na_2SO_4		360	13	32	31 000	38 000	2.1
		380	39	37.5			1.67
		428	175	48.5			1.06
BeO with addition of 0.32% Na_2SO_4		360	20	33.5	22 000	30 000	2.0
		382	62	36			1.78
		406	94	38.5			1.60
		426	175	48.5			1.06
BeO with addition of 0.55% Na_2SO_4		358	27.3	30	17 000	29 000	2.3
		382	99	34.3			1.92
		402	126	35.4	17 000	29 000	1.82
		432	167	39.4			1.54
BeO with addition of 2.04% Na_2SO_4		384	44	19.5	32 000	36 000	4.1
		406	86	23			3.3
		430	115	29			2.45

rates of feed of alcohol the order of the reaction of decomposition of isopropyl alcohol is between zero and unity and is nearer to the former. This fact makes it possible to calculate activation energies without any great error from experimental data on the rate of gas liberation at various temperatures with a given rate of feed of alcohol. In all succeeding tables the results on the rate of liberation of gas are given for a rate of feed of alcohol of 0.25-0.33 ml/minute. From the graphs in Fig. 4 we constructed graphs for the relation between the extent of decomposition of the alcohol (as a percentage of complete decomposition) and 1/T, and from these – graphs for time of contact (at constant conversion) against 1/T. Activation energies of dehydrogenation E calculated in this way for BeO varied, according to the coverage, from 23,000 to 29,000 cal/mole; for ZnO they were 11,000-19,000 cal/mole. The values of dehydrogenation activation energy given in Tables 1 and 2 for these samples are 25,000 and 13,000 cal/mole, respectively, which coincide with values obtained by a more accurate method of calculation; this convinces us that the use of such values is valid.

Figure 5 gives data on the activity of BeO (total gas liberation) and Fig. 6 on its selectivity (yield of unsaturated hydrocarbons) as functions of the Na_2SO_4 content of the BeO. Table 2 gives the experimental results on the catalytic decomposition of isopropyl alcohol over MgO and ZnO. These catalysts have been studied by many investigators [1-5] and we therefore investigated them in less detail.

The dehydrogenation activation energies of isopropyl alcohol over MgO and ZnO were calculated from the straight lines in Fig. 7. It must be pointed out that in reaction in the adsorption layer on ZnO the character of the decomposition of isopropyl alcohol was substantially different and the desorbed products contained a preponderance of propene and water, i.e. dehydration products. In this case the surface coverage was 2-8%

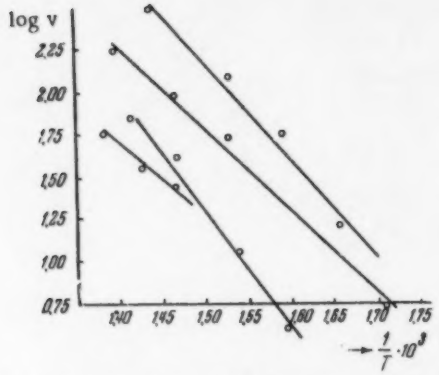

Fig. 1. Relation between the logarithm of the rate of dehydrogenation of isopropyl alcohol and 1/ T for various samples of beryllium oxide.

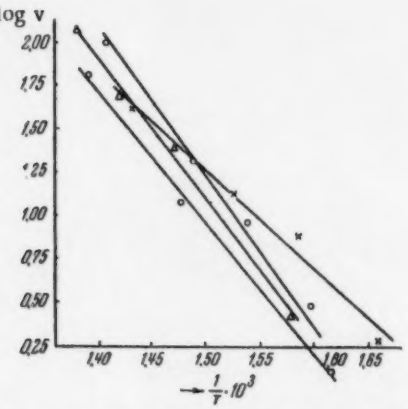

Fig. 2. Relation between the logarithm of the rate of dehydration of isopropyl alcohol and 1/ T for various samples of beryllium oxide.

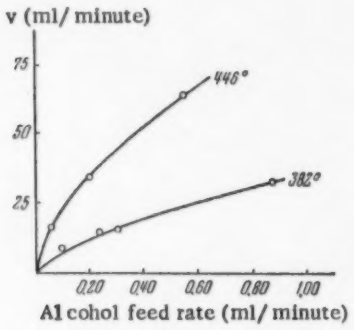

Fig. 3. Relation between the rate of dehydrogenation over BeO and the rate of feed of isopropyl alcohol.

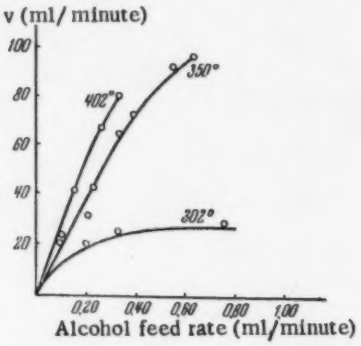

Fig. 4. Relation between the rate of dehydrogenation over ZnO and the rate of feed of isopropyl alcohol.

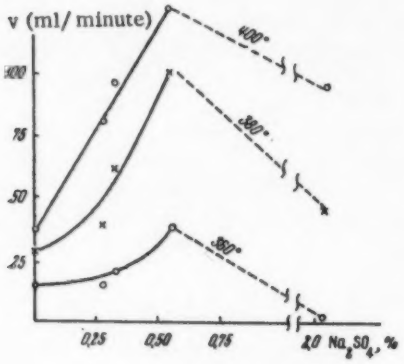

Fig. 5. Relation between catalytic activity of BeO and Na_2SO_4 content.

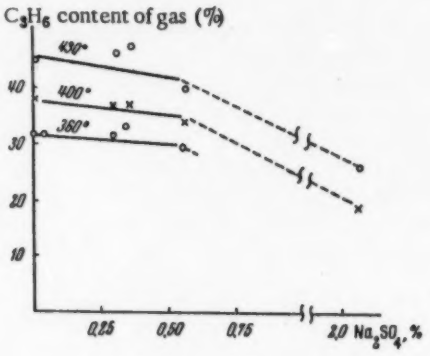

Fig. 6. Relation between selectivity of BeO (degree of dehydration) and Na_2SO_4 content.

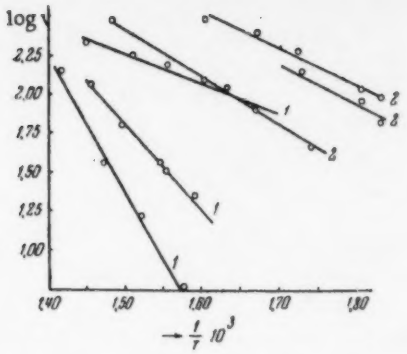

Fig. 7. Determination of the activation energy for the dehydrogenation of isopropyl alcohol over: 1) MgO; 2) ZnO.

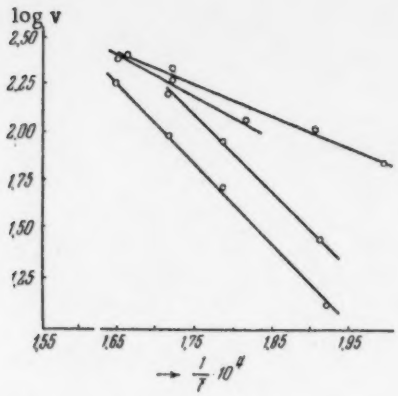

Fig. 8. Determination of the activation energy for the dehydrogenation of isopropyl alcohol over various samples of CdO.

Under certain conditions the extent of dehydrogenation increased with rise of temperature. A similar effect was observed for ethanol over ZnO by Keier [8]. Work is now being carried out with the object of defining the exact causes of this change in the course of the decomposition of the alcohol over ZnO.

TABLE 2

Experimental Results on the Decomposition of Isopropyl Alcohol Over Magnesium and Zinc Oxides.

Catalyst	Specific surface (sq.m/g)	Temperature (°C)	Rate of gas liberation (ml per ml of alcohol per minute)	Propene content of gas (%)	Act. energy for dehydrog. E_{H_2} (cal/mole	Act. energy for dehydrat. E_{H_2O} (cal/mole)	Selectivity coefficient $\frac{[H_2]}{[C_3H_6]}$
MgO from sulfate via hydroxide	153	328	84.5	2.4	10 000	14 000	41
		372	167	2.6			37
		392	182	3.0			32
		420	209	3.2			30
MgO from carbonate	61	360	6.4	4.0	28 000	32 000	24
		385	18	4.9			19.5
		405	39	5.9			16.0
		434	134	6.1			15.3
MgO from nitrate via hydroxide		356	24	2.3	21 000	30 000	43
		370	41.5	4.3			22
		398	67	8.2			11.2
		416	125	10.9			8.2
ZnO from sulfate via hydroxide	16.4	256	60.5	2.4	13 000	26 000	41
		280	132	2.7			36
		304	231	6.4			14.6
		334	357	7.0			13.3
		344	320	7.5			12.3
ZnO from nitrate via hydroxide		260	112	0.9	12 000	18 000	110
		278	125	1.3			76
		308	207	1.4			70
		324	258	1.7			58
		354	283	2.0			49
		380	293	2.2			44
		406	315	2.6			37
ZnO from nitrate via hydroxide (another preparation)		302	58	4.0	13 000	18 000	24
		340	112	7.0			13.3
		350	124	8.0			11.5
		402	294	9.5			9.5

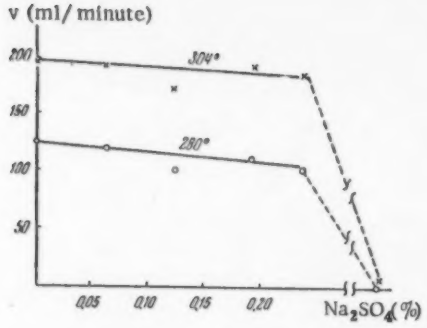

Fig. 9. Relation between catalytic activity of CdO and Na_2SO_4 content.

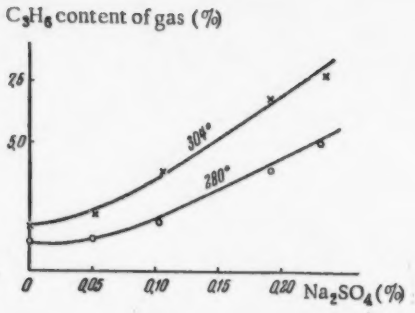

Fig. 10. Relation between selectivity of CdO (degree of dehydration) and Na_2SO_4 content.

TABLE 3

Experimental Results on the Decomposition of Isopropyl Alcohol Over Cadmium Oxide.

Catalyst	Specific surface (sq. m/ g)	Temperature (°C)	Rate of gas liberation (ml per ml of alcohol per minute)	Propene content of gas (%)	Act. energy for dehydrog. E_{H_2} (cal/ mole	Act. energy for dehydrat. E_{H_2} (cal/ mole	Selectivity coefficient $\frac{[H_2]}{[C_3H_6]}$
CdO from nitrate via hydroxide	6.0	190	10	0.6	10 000	24 000	160
		230	15	1.0			99
		286	33	1.2			82
		374	152	5.6			16.8
CdO from nitrate via hydroxide (another sample)	7.2	220	57	1.1	8 000	17 000	90
		250	106	1.2			82
		304	210	1.45			68
		330	235	2.4			41
CdO from sulfate via hydroxide	6.2	244	36	0.5	11 000	19 000	200
		276	124	1.0			99
		302	200	1.2			82
		334	237	1.5			66
		382	285	4.4			22
CdO from nitrate		286	26	1.0	16 000	24 000	99
		310	80	1.5			66
		336	159	2.1			47
		358	258	4.4			22
CdO from carbonate	6.1	246	13	—	14 000	24 000	—
		276	54	1.0			99
		310	96	1.1			90
		334	192	1.2			82
		362	235	2.7			36
CdO with addition of 0.063% Na_2SO_4		256	29	0.6	10 000	17 000	166
		276	91	1.2			82
		304	151	1.9			52
CdO with addition of 0.12% Na_2SO_4		224	61	1.3	10 000	17 000	76
		252	73	1.9			52
		284	114	2.2			44
		304	194	3.6			27
		324	243	3.9			25
CdO with addition of 0.19% Na_2SO_4		236	16.4	0.8	20 000	29 000	124
		260	94	2.2			44
		276	118	3.6			27
		302	192	7.0			13.3
CdO with addition of 0.23% Na_2SO_4		222	12.5	0.5	19 000	22 000	199
		258	25	1.5			66
		280	101	5.1			18.6
		308	182	7.8			11.8

Table 3 gives results on the catalytic decomposition of isopropyl alcohol over cadmium oxide, both pure and also with additions of Na_2SO_4. It must be pointed out that CdO, unlike the other oxides, did not give reproducible results when we returned from high temperatures of decomposition to low. This is to be explained by the fact that, under the conditions of the experiment at about 300° and above, there occurred reduction of CdO to metal and sublimation of metallic Cd (formation of a mirror in the lower part of the apparatus). In all experiments, therefore, we began with measurements of catalytic activity at low temperatures, passed on to high temperatures, and at this point terminated the study of the given sample without returning to low temperatures.

The straight lines from which the activation energies were calculated for the dehydrogenation of isopropyl alcohol over CdO are given in Fig. 8. Figure 9 gives data on activity (total gas liberation) and Fig. 10 on selectivity (propene content of gas mixture) as a function of the Na_2SO_4 content of cadmium oxide.

The oxide of the heaviest element of this group HgO is readily reduced to metallic mercury in an atmosphere of isopropyl alcohol already at 100° and above. In the first few moments, while the mercuric oxide has still not been reduced completely to metal, a large amount of gas – consisting almost entirely of hydrogen – is liberated. In view of the low specific surface of HgO (less than 5 sq.m/g), we may assert that it is highly active.

DISCUSSION OF RESULTS

The experimental results given in Table 1-3 show that over most of the oxides studied the decomposition of isopropyl alcohol proceeds mainly in the dehydrogenation direction:

$$C_3H_7OH \rightarrow CH_3COCH_3 + H_2.$$

In the temperature range studied (312-446°), only over BeO did both dehydrogenation and dehydration of isopropyl alcohol proceed to comparable extents.

The variation in activity and selectivity among samples of a given catalyst prepared in different ways is less than the variation found among the different oxides. Activation energies vary between comparatively narrow limits: the extreme values of activation energy for a given catalyst differ by 5-8 kcal/mole. Only a sample of MgO obtained by precipitation of the hydroxide from a solution of the sulfate and subsequent calcination was exceptional – it had anomalously low activation energies, namely, 10,000 cal/mole for dehydrogenation and 14,000 cal/mole for dehydration (for other samples these values were 21,000-28,000 and 30,000-32,000 cal/mole, respectively). The same catalyst gave an anomalously low degree of dehydration (2-3%) in the range of temperatures studied and it had very high specific surface and catalytic activity. The ratio of degrees of dehydration and dehydrogenation over various samples depends not only on the difference $E_{H_2O} - E_{H_2}$, but also on the ratio k_{0H_2O}/k_{0H_2}, because in certain cases (see, for example, the first two samples of BeO in Table 1) catalysts with different activation energies and similar specific surfaces give degrees of dehydration and dehydrogenation that are close in magnitude. Samples of BeO, MgO, and CdO obtained from the hydroxides are more active and give a higher degree of dehydrogenation than samples obtained by calcination of the carbonates and nitrates, but, if we take account of the fact that these samples have also greater surface areas, the differences in activity are found to be much less. The specific catalytic activity, i.e. yield of product calculated for unit surface [9], was not calculated here because the use of this concept is possible only for catalysts having the same activation energy, which clearly does not apply in the present case. The intersection of Arrhenius straight lines not only for different oxides, but also for different preparations of the same oxide, indicates that the catalysts that are the most active in one temperature range become the least active in another.

Study of the effect of additions of Na_2SO_4 on the catalytic activity of BeO and CdO showed that the effect is different in the two cases. In the case of CdO (Figures 9 and 10), with increase in the Na_2SO_4 content of the catalyst there is a great fall in activity and increase in the yield of unsaturated hydrocarbons. In the case of BeO (Figures 5 and 6), with increase in the Na_2SO_4 content the activity rises somewhat, attains a low maximum, and falls (as in the case of CdO) at high Na_2SO_4 contents, probably owing to blocking of the surface. In the course of these changes the yield of unsaturated hydrocarbons changes comparatively slowly, and it diminishes appreciably only when the Na_2SO_4 content is high. It is possible that the differences in the catalytic properties of different samples are due to effects of impurities.

Examination of all the experimental results shows that, in spite of variations among samples prepared in different ways, with increase in atomic weight in the elements of Group IIB, the catalytic activity of the oxide – BeO, MgO, ZnO, CdO, and HgO – increases, the content of unsaturated hydrocarbons produced under the given experimental conditions diminishes, and the activation energies for dehydration and dehydrogenation fall (more for dehydrogenation than for dehydration). Activation energies for dehydrogenation vary within the following limits (cal/mole): BeO – 21,000-29,000; MgO – 21,000-28,000 (with exception discussed above); ZnO – 12,000-13,000; CdO – 8,000-16,000; HgO appears to occupy the last place in this series, for the temperature at which dehydrogenation of isopropyl alcohol begins over HgO (100°) is much lower than over the other oxides. In the case of activation energies for dehydration the corresponding series is (cal/mole): BeO – 32,000-36,000; MgO – 30,000-32,000; ZnO – 18,000-26,000; CdO – 17,000-24,000.

For all the oxides studied the activation energy for dehydrogenation was lower than the activation energy for dehydration. It must be noted, however, that at low surface coverage (2-8%) the decomposition of isopropyl alcohol differs in character (selectivity), as indicated above; this probably arises from surface heterogeneity, which causes the dehydrogenation catalyst to acquire dehydrating properties. In this case the laws of catalyst selection may be quite different.

Oxides of Group IIB differ in properties from those of Group IIA mainly in respect of the magnitude of the absolute activity. The preexponential factors k_0 of the Arrhenius equation are higher by a factor of 10^2-10^3 for Group IIB oxides CdO and ZnO than for the Group IIA oxides CaO, SrO, and BaO of similar molecular weight. The laws governing the changes in catalytic activity and activation energies for dehydration and dehydrogenation with increase in molecular weight are identical for Group IIB and Group IIA oxides. In their behaviors in this reaction BeO and MgO correspond to the first members of the series of Group IIB oxides arranged with respect to change in catalytic properties and not to the Group IIA series.

In the main, our results are in accord with concepts derived from the classification of catalytic processes [10]. Dehydrogenation appears to be a process of the oxidation-reduction (electronic) type. To a certain extent, therefore, the dehydrogenating properties of oxides must vary with their electronic properties. It can be seen that with increase in molecular weight the Group IIB oxides not only have increased catalytic activity, but also have more pronounced "semiconductor" properties, such as intensity of color, readiness of reduction, and electrical conductivity (in the range of temperatures in which catalysis occurs in our experiments, we are probably dealing mainly with intrinsic conductivity and not with conductivity due to impurities [11]).

A comparison of the data on the dehydrating properties of oxides with our data on the acid-base properties of the same oxides [12] shows that there is a symbatic relationship between dehydrating and acidic properties. It is probable that dehydration is a process of the acidic type and is determined by the direct transfer of a proton. The acidic properties of Group IIB oxide catalysts are not strongly marked, and this is reflected in their feeble dehydrating power. Only beryllium oxide, which is a compound of a metal from the beginning of Group II and has amphoteric properties, has appreciable dehydrating power.

SUMMARY

1. A study was made of the catalytic activity and selectivity of oxides of Group IIB metals – BeO, MgO, ZnO, CdO, and HgO – in the decomposition of isopropyl alcohol in a flow system at atmospheric pressure in the temperature range 190-454°.

2. Over MgO, ZnO, CdO, and HgO under the conditions studied, the predominant reaction is the dehydrogenation of isopropyl alcohol. Over BeO dehydrogenation and dehydration proceed to about the same extent. In all cases rise in temperature results in an increase in the extent of dehydration, i.e. the activation energy for dehydration is higher than that for dehydrogenation.

3. Variations in the method of preparing the oxides greatly affect their catalytic properties – activity and activation energies for dehydration and dehydrogenation – and also their specific surfaces. However, these changes do not obscure the differences due to the position of oxide-forming element in the periodic system. The concept "specific catalytic activity" is not applicable to the characterization of the relation between the catalytic activity of an element and the position of this element in the periodic system.

4. Impurities originating during the preparation of the catalyst or introduced artifically (e.g. SO_4^{2-})

substantially affect its activity and the direction of the process.

5. When the catalytic properties of oxides of Group II metals are considered in relation to the positions of the metals in the periodic system it is found that catalytic activity increases with increase in the atomic weight of the metal. There is a simultaneous increase in the extent of dehydrogenation of the alcohol, and the activation energies for dehydration and dehydrogenation fall.

6. When the decomposition of the alcohol takes place in the adsorption layer at low surface coverage (2-8%), the course of the reaction may be different. Over ZnO under these conditions, dehydration predominates over dehydrogenation.

7. It is suggested that there is a relationship between the course of the decomposition of isopropyl alcohol and the electronic and acid-base properties of the catalyst.

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** [See C. B. translation].

APPLICATION OF ULTRA-THIN SECTIONING IN THE ELECTRON-MICROSCOPY OF CATALYSTS

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Up to now electron microscopy has found only limited application in the direct study of catalysts and adsorbents owing to difficulties in the preparation of samples in a form in which they can be examined in the electron microscope. The objects examined have been mainly model systems, such as metals in the mass [1] and smoke deposits, which are not used to any extent in catalysis, and various colloidal systems, such as certain colloidal catalysts in photographic emulsions and precipitates of hydroxides and salts. An examination of recent literature [3-7] on electron microscopy gives one reason to suppose that the lack of progress in the application of electron microscopy to the study of dispersed and polycrystalline solids is to be explained by the extreme crudity and scarcity of the methods available for the preparation of a substance for investigation.

These methods, in their application to solids, can be classified as direct and indirect. Direct methods are those which permit the direct observation of an object, and they include methods of preparing samples from suspensions [2, 3], by application to a film in a highly comminuted form, by grinding so as to give a film-forming material, and also several methods proposed recently under the name of "dry methods" [4], which also consist in mechanical grinding of the material and collection of the finest component of the aerosol on a film.

The indirect methods include the preparation of various one-stage and two-stage replicas, i.e. castings taken from the surface of the object under study, which are subsequently examined under the electron microscope. These methods have been described in detail in various articles. For example, it has recently been suggested that a solution of a polyamide in formic acid should be used instead of collodion or methyl methacrylate in the preparation of replicas [5]. Various methods have been developed for taking two-stage replicas by shadowing the collodion or methacrylate film with silicon or quartz and then dissolving away the organic support [2, 6, 7]. Shadowing of replicas with various metals often facilitates examination and, particularly, interpretation of electron micrographs.

From the point of view of the investigation of catalysts, which are generally highly dispersed polycrystalline solids formed into a definite shape, the methods discussed above suffer from serious defects. Thus, the above-mentioned "direct" methods cannot, of course, reveal the detailed internal structure of the formed catalyst particle in a reliable manner because these methods are based on the destruction of this particle.

Apart from being indirect, the replica method also gives a limited characterization of the catalyst particle, since it reveals only the visible geometric surface of the grain and gives no idea of the internal structure, which may differ appreciably from the structure of the geometric surface owing to the effects of mechanical (grinding, chipping) and chemical (hydration, oxidation) action on the latter. We consider that the need for supplementing the information given by replicas with data on the internal structure of the catalyst grain is quite obvious, especially when we formulate clearly what information we require from the electron microscopy of catalysts.

From the point of view of the electron microscopy of catalysts, our ideal requirement is the possibility of direct observation of a) the form and dimensions of the elementary crystals; b) the character of their aggregation; c) the character of the distribution of phases; d) the porous structure of the grain, the observations ranging from the fine (less than 100 A) to the coarse pores, which is possible by the use of different magnifications.

All these data are important because they are related not only to the activity of the catalyst, but also to the mechanical strength of the grain, which often determines the possibility of using the given catalyst in practice.

In our examination of existing methods of preparing solids for electron-microscopic investigation, we turned our attention on the surprising fact that the extensive experience gained in the normal microscopic and electron-microscopic investigation of biological objects has been left completely out of consideration. Among the methods described for the electron-microscopic investigation of catalysts and adsorbents, we did not find the method of examining or photographing thin or ultra-thin sections. Such a method, however, applied to catalysts and adsorbents could give very much information and might satisfy all the requirements listed above. Quite naturally, therefore, we tried to verify the possibilities of the use of the microtome, and the results we obtained were quite satisfactory.

EXPERIMENTAL

Owing to the much higher resolving power (and shorter wavelength) of the electron microscope, as compared with the optical microscope, the demands made with respect to the sectioning of biological objects are much more exacting. Microtomes of modern design can produce ultra-thin sections ranging down to 0.01 μ, or even still thinner. Unfortunately, there are no Soviet microtomes of this type.

The literature indicates that modern microtomes incorporate the following features or modifications of design:

1) replacement of the mechanical advancement of the block to the knife by readily controllable and much more sensitive thermal advancement;

2) replacement of the steel knife by a glass knife – a freshly made splinter of plate glass set at a definite angle; and

3) the use of antivibration and centering devices on the object carrier.

In modern microtomes designed for the preparation of ultra-thin sections, the knife is rigidly fixed, and the object is fed to the knife by turning the disk of the object carrier, the advancing movement of the object carrier being effected by the regular thermal expansion of the advancing unit. As indicated by Jung [8], design of an object carrier free from vibration should be based on the use of glass surfaces ground together into optical contact; with a lubricant of suitable viscosity the mutual centering of the driving (fixed to the advancing unit) and driven glass disks is effected automatically, rapidly, and reliably. This principle in its general form was used by us in the design and construction of a microtome for the preparation of ultra-thin sections (Fig. 1); this embodied also the other principles of design enumerated above. Owing to the absence in the literature of detailed descriptions of various components of this precise and sensitive apparatus, many of the parts were of original design. We have given a more detailed description of the instrument in a special article [9].

Testing of the apparatus with the aid of an accurate indicator showed that, owing to highly sensitive control of the heat supply, the advancement of the object against the knife could be regulated down to 1 μ per minute; sections of various thicknesses could be obtained by varying the rate of rotation of the object carrier. Thus, at 130 turns per minute with an advancement of 1 μ per minute, sections less than 0.01 μ in thickness, i.e. of the order of 100 A, were produced in the form of a continuous ribbon; it was difficult to distinguish these sections on the surface of water with an MBI-2 binocular magnifier at maximum magnification.

Any attempt to prepare sections directly from a grain of catalyst could not, of course, give good results because of its brittleness and because of the comparatively low binding forces between its component particles: we should expect to obtain only the same result as in the above-described dry methods of preparation.

We prepared our sections by the method employed in biology, i.e. by the preparation of "blocks": the sample was placed in a mixture of methyl and butyl methacrylates (1:3), which was polymerized at 50° for 24-48 hours, the resulting block being then sectioned on the microtome. Owing to the elasticity and viscosity of the methacrylate embedding medium, crumbling and disintegration of the object was prevented and the structure of the layer cut from the grain of catalyst was fully preserved in the section. We must point out that obtaining good results depends greatly on the quality of the glass knives, in the making of which several

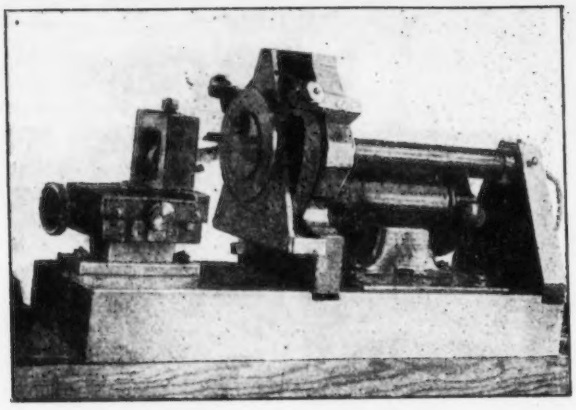

Fig. 1.

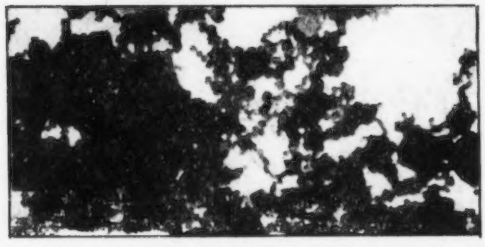

Fig. 2.

difficulties are met: the knife must be a fresh even splinter made at an angle of about 45°.

We showed that the structure of very thin sections can be observed and photographed directly in the electron microscope without removal of the cementing film of methacrylate polymer (Fig. 2). When the film thickness is of the order of 0.01 μ, the methacrylate embedding medium can be very readily dissolved in aqueous acetone or other (nonaqueous) organic solvents so that a section freed from methacrylate polymer can be obtained on the grid of the object carrier of the electron microscope (Fig. 3).

Figure 2 shows an example of the results obtained by this method – an electron micrograph of a mixed $NiO-Al_2O_3$ catalyst prepared by coprecipitation and subsequent calcination at 400°. This photograph shows that the picture obtained in this way does in fact convey the structure of the catalyst grain, the character of the component particles, and the dimensions of the pores. The magnification is 21,000.

A considerably more highly dispersed MgO catalyst, the crystals of which had dimensions estimated by X-ray analysis at 50-60 A, gave the picture (magnification 16,000) in Fig. 3, the characteristic feature of which is the high homogeneity with respect to the dimensions of the crystals and probably also of the pores. The form of the crystals is not seen sharply; in all probability this arises mainly from the fact that their dimensions lie at the limit of the resolving power of the EM-3 electron microscope. It may be noted also that this photograph shows that the object is of fairly regular, small thickness and readily transmits the electron beam; also, and this is very important, there is an absence of confusion from lower layers such as generally occurs in other methods.

Summarizing, we may state that the method of preparing ultra-thin sections and their investigation under the electron microscope is applicable not only to biological objects, but also to solids such as catalysts and adsorbents. There are some questions of method which require further study. Thus it will be necessary to experiment with catalysts and adsorbents differing in degree of hardness and objects containing crystals of

Fig. 3.

various sizes, and it will probably be necessary to determine the effect of some other properties of catalysts. However, it is already clear that the method of preparing ultra-thin sections provides substantial supplementation of the methods used at present for the preparation of solids for electron microscopy.

SUMMARY

1. It is proposed that the method of preparing ultra-thin sections be applied to the electron-microscopic investigation of the structure of catalysts and adsorbents, and examples of the results obtained are given.

2. For the first time in the USSR, a microtome has been designed and constructed which will give sections of thickness not exceeding 0.01 μ.

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PROPERTIES OF A NICKEL CATALYST PREPARED BY THE DECOMPOSITION OF A DOUBLE MAGNESIUM NICKEL FORMATE

L. Kh. Freidlin, A. A. Balandin, and K. G. Rudneva

Several types of nickel catalysts for low-temperature hydrogenation are now known. However, only one type – Raney nickel – has found extensive application. The others are scarcely used, partly because of their relatively low activities and partly because of difficulties of preparation. Recently, Langenbeck and coworkers [1] prepared several catalysts for low-temperature hydrogenation by the decomposition of double magnesium nickel and nickel zinc formates and oxalates at 350° in a stream of hydrogen. Still more active catalysts were prepared by Danes and Jiry [2] by decomposition of double oxalates in a high vacuum at 430-450°. Catalysts of this type are highly active and simple to prepare. This new method of preparing active nickel catalysts is important also in another respect: it has been very difficult in practice to prepare a catalyst for low-temperature hydrogenation from spent or deactivated Raney nickel, but nickel from a spent nickel catalyst can now be readily converted via the nitrate into a catalyst for low-temperature hydrogenation. It was considered to be of interest to make a more extensive investigation of some properties of these catalysts: activity, thermal stability, and hydrogen content.

EXPERIMENTAL

As Rienäcker and coworkers [3] have shown, the highest activity (per unit weight) is possessed by Ni-MgO catalysts containing 20-50% of nickel. In our experiments we used a catalyst containing equal amounts by weight of Ni and MgO. Magnesium oxide (30 g) was dissolved in formic acid, and the solution was mixed with an aqueous solution of 95.5 g of nickel formate dihydrate. The mixed salt obtained after evaporation was ground carefully in a mortar and reduced in a stream of hydrogen for two hours at 350°. The catalyst obtained was cooled to room temperature in the stream of hydrogen and immersed in water.

The activities of samples of catalyst were evaluated from the rates of hydrogenation of approximately equimolecular amounts (corresponding to the consumption of 50 ml of hydrogen) of various substances in presence of the catalyst. Styrene, piperylene, acetals, and organosilicon compounds were hydrogenated in dioxane (free from peroxides), and other substances in 96% ethanol (10 ml). The reaction was carried out at 20° in a hydrogenation flask, length 180 mm and diameter 30 mm. The length of sweep was 10.5 cm and the frequency of shake was 700 per minute. It was found that these conditions ensured that reaction proceeded in the kinetic region [4]. Before reaction the catalyst was washed with 10 ml of the appropriate solvent (dioxane or ethanol) with shaking. Electrolytic hydrogen was used.

For comparison purposes, simultaneously with work on the Ni-MgO catalyst activity measurements were made with Raney nickel in the same reactions and under similar conditions. The Raney catalyst was prepared by leaching a 50% alloy with 20% sodium hydroxide at 105° for two hours. In the graphs, kinetic curves for hydrogenation with an Ni-MgO catalyst are denoted by circles (○) and those for hydrogenation with a Raney catalyst by spots (●). In the experiments represented by kinetic curves h and i in Fig. 1, a and e in Fig. 3, and the curves in Figures 4-6 and 8, a sample of catalyst containing 0.5 g of nickel was used, and in the other experiments – 1 g of nickel. A new portion of catalyst was used in each experiment. All operations were carried out under conditions which made it impossible for the catalyst to come into contact with air.

The activity of an Ni-MgO catalyst was studied for the hydrogenation of dienes, compounds containing a double or triple carbon-carbon bond, and oxygen- and silicon-containing compounds. The graphs are kinetic

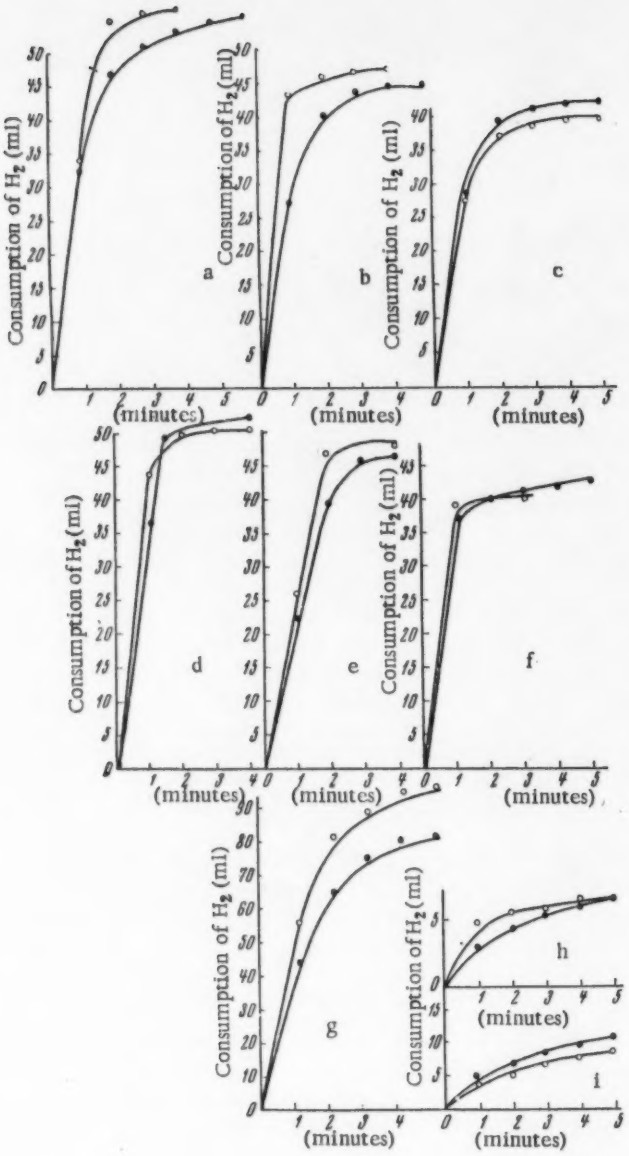


Fig. 1.

curves characterizing the rate of hydrogenation of these compounds in presence of Ni-MgO and Raney nickel catalysts.

As will be seen from Fig. 1, for all the compounds represented hydrogenation proceeds at approximately the same rate over the two catalysts; the compounds are styrene (1a), the acetal $CH_3CH(OCH_3)OC(CH_3)_2CH=CH_2$ (1b) (C = C), mesityl oxide (1c) (C = C), hexyl vinyl and phenyl vinyl ethers (1d and 1e), 1-heptyne (1f), the

acetal $CH_3CH(OCH_3)OC(CH_3)_2C \equiv CH$ (1g) (C ≡ C), benzophenone (1h) (C = O), and acetophenone (1i) (C = O),*

Benzaldehyde (Fig. 2a) and 2-butanone (2b) are hydrogenated more rapidly over Ni-MgO than over Raney nickel.

In the hydrogenation of cinnamyl alcohol and cinnamic acid (Figs. 3a and 3b), piperylene, cyclohexene,** diphenylacetylene, and 2-octene (Figs. 3c to 3f), and also of the C = C bond of the organosilicon compound $CH_3Si(CH_2)_3OCH = CH_2$ (Fig. 3g), the activity of the Ni-MgO catalyst was considerably less than that of Raney nickel.

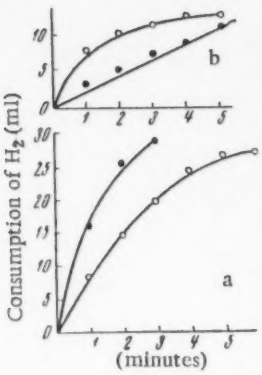
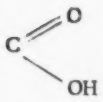


Fig. 2.

It follows from the results also that the rates of hydrogenation of various functional groups over an Ni-MgO catalyst are generally in the same order as over Raney nickel. Hydrogen adds most rapidly to an ethylenic bond. Of the conjugated dienes, cyclohexadiene is hydrogenated more rapidly than piperylene. Heptyne is hydrogenated more rapidly than diphenylacetylene, and benzaldehyde more rapidly than acetophenone, benzophenone, or butanone. The double bond of compounds containing a silicon atom or carboxy group is hydrogenated least rapidly: this is probably to be explained by the fact that adsorption on Ni-MgO of the molecule being hydrogenated in the



group or silicon atom competes with adsorption of the C = C group on the metal component of the catalyst.

Experiments were carried out on the reduction of a layer of the mixed salt, varying in depth and 150 ml in length, in a tube 20 mm in diameter. It was found that the catalysts obtained by the decomposition of two different portions (7 g and 46 g) of mixed formate differed little in activity. It must be mentioned that in the course of the reaction, during shaking, the catalyst formed into a turbid suspension and the liquid being hydrogenated was with difficulty separated from it by filtration. It is possible that samples of high nickel content (and prepared from oxalates) would not have this shortcoming.

For the investigation of thermal stability, the catalyst in the form of a paste was placed in a quartz tube heated in an electric furnace. Throughout the experiments nitrogen was passed through the tube at a rate of 4 liters per hour. The nitrogen was first freed from oxygen and moisture by passage over heated copper turnings, through pyrogallol solution, and then through sulfuric acid. Heating of the furnace to the temperature of the experiment did not take more than 30-40 minutes, and this time was not included in the duration of the experiment. At the end of the experiment the catalyst was cooled to room temperature and transferred in a stream of nitrogen into alcohol or water. In these and subsequent experiments, the activities of samples of catalyst were characterized by the rate of absorption of hydrogen in the hydrogenation of 0.2495 g of phenyl vinyl ether in 10 ml of 96% ethanol at 20°. It follows from Fig. 4 that after two hours' heating at 235° and 400° (Curves 2 and 3) the catalyst completely retained its initial activity (Curve 1). Only after two hours at 550° the activity of the catalyst fell sharply (by a factor of 15-20) (Curve 4). Hence, the thermal stability of this catalyst is about the same as that of Raney nickel [5].

It has been shown previously that nickel catalysts for low-temperature hydrogenation generally contain considerable amounts of chemically active hydrogen [6]. In order to determine the hydrogen content of the catalyst under study, it was treated with a 3% solution of p-benzoquinone in dioxane with shaking for one hour at 60° in an atmosphere of nitrogen. Analysis of the reaction product for hydroquinone content showed that the catalyst contained 65 ml of hydrogen per gram of nickel. The hydrogen content of Raney nickel catalyst

* Reaction rate is given for the first five minutes.

** The subsequent discussion indicates that cyclohexadiene is probably meant here. – Publisher.

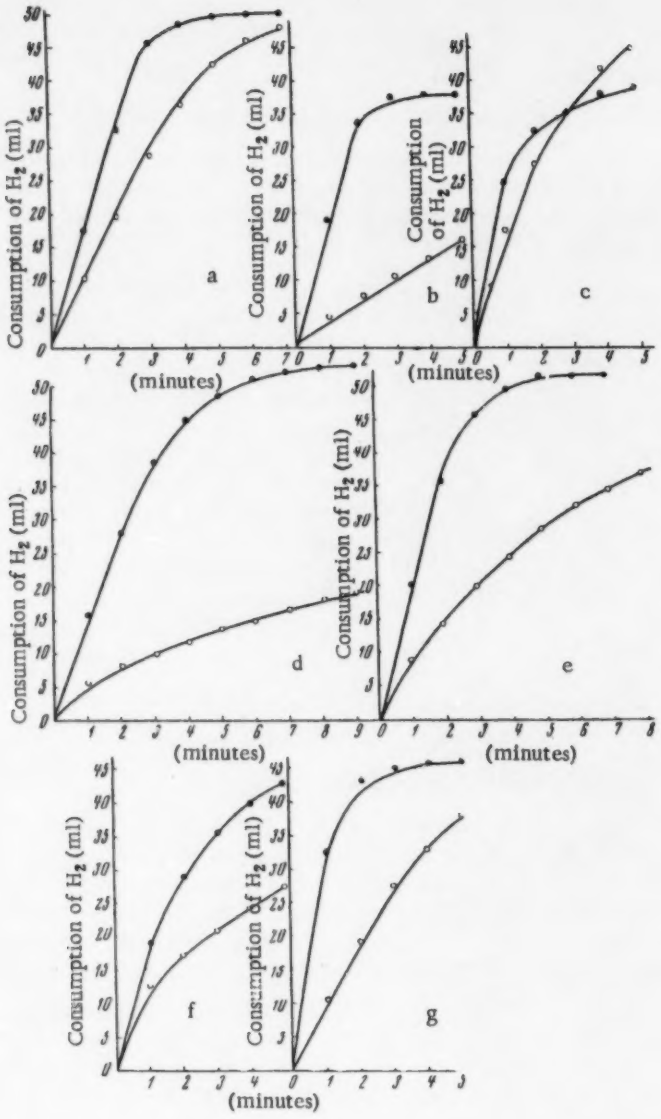


Fig. 3.

is about the same. After removal of hydrogen from the catalyst it was inactive.

As will be seen from Fig. 5, the optimum temperature for the reduction of the mixed salt (for a two-hour heating) is in the range 350-450° (Curves 2 and 3). Lowering of temperature to 250° or raising it to 550° (Curves 1 and 4) results in a much lower activity. Reduction in the rate of passage of hydrogen from 4.5 to 3 or 1.8 liters per hour in the reduction of 7 g of mixed salt has almost no effect on the activity of the catalyst (Fig. 6, Curves 1, 2, and 3). With further reduction in the rate of passage of hydrogen to 0.8 liter per hour, a catalyst of lower activity is obtained (Curve 4).

Experiments were carried out also on the decomposition of the mixed formate in absence of hydrogen. It will be seen from Fig. 7 that nickel obtained by decomposition of the double salt for two hours at 350° in an atmosphere of nitrogen (Curve 2) had approximately one twenty-fifth of the activity of the nickel obtained

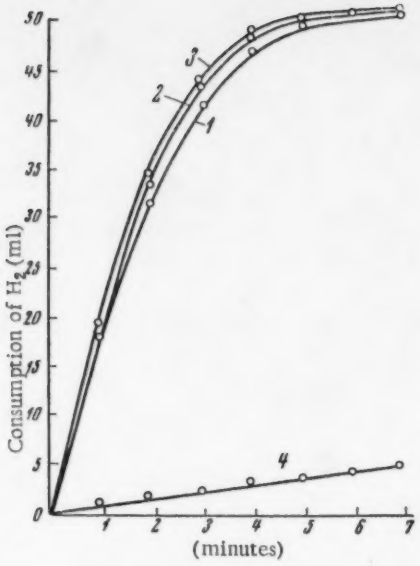


Fig. 4.

by decomposition in a stream of hydrogen (Curve 1). When the sample of low activity was subsequently treated with hydrogen for two hours at 350° it acquired normal activity (Curve 3).

It is known that a Raney nickel catalyst can be oxidized at 350-400° and that the resulting nickelous oxide can then be rereduced at this temperature with hydrogen with re-formation of a catalyst for low-temperature hydrogenation [7]. An active Ni-MgO catalyst was oxidized with atmospheric oxygen for two hours at 400° and then reduced with hydrogen for two hours at 350°. As will be seen from Fig. 8 (Curve 2), the activity of the regenerated catalyst was equal to that of the original sample (Curve 1). Hence, like other nickel catalysts, this catalyst can be regenerated by oxidation and subsequent reduction.

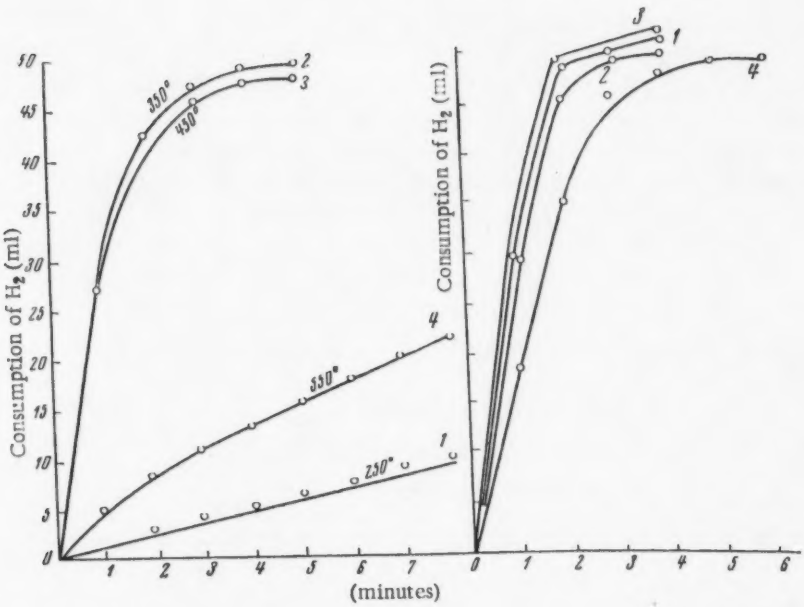


Fig. 5, 6.

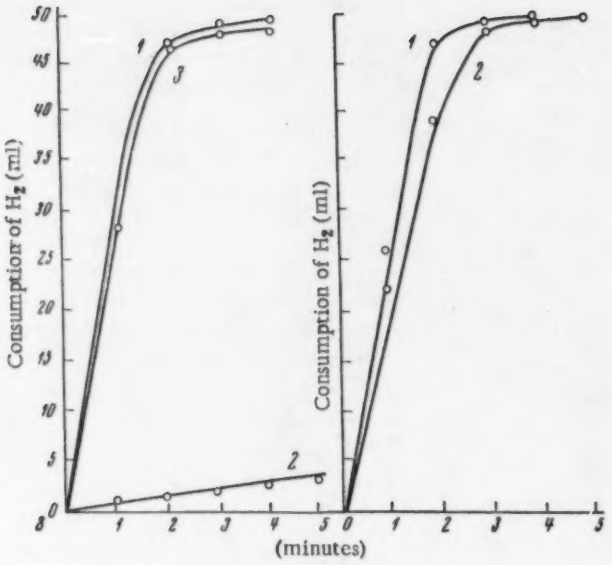


Fig. 7, 8.

SUMMARY

1. A comparative investigation was made into the properties of a Raney nickel catalyst and an Ni-MgO catalyst prepared from a mixed magnesium-nickel formate in hydrogenation reactions at room temperature.

It was shown that vinyl ethers, 1-heptyne, mesityl oxide, styrene, acetals having double and triple bonds, acetophenone, and benzophenone are hydrogenated over Ni-MgO catalyst and Raney nickel at about the same rates. Butanone and benzaldehyde are hydrogenated more rapidly over an Ni-MgO catalyst, but for the hydrogenation of 2-octene, cinnamyl alcohol, cinnamic acid, piperylene, cyclohexene [or cyclohexadiene?--see previous note – Publisher], diphenylacetylene, and organosilicon compounds the activity of the Ni-MgO catalyst is lower than that of Raney nickel.

2. It was found that with respect to thermal stability, content of sorbed hydrogen, and possibility of regeneration by oxidation and subsequent reduction this catalyst is similar to Raney nickel.

A catalyst obtained by decomposing the mixed salt in an atmosphere of nitrogen is of low activity.

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* [See C. B. translation].

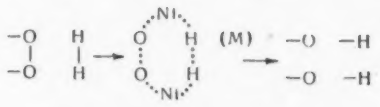
KINETICS OF THE CATALYTIC REDUCTION OF ORGANIC PEROXIDES AND HYDROPEROXIDES

COMMUNICATION 1. HYDROGENATION OF α, α-DIMETHYLBENZYL HYDROPEROXIDE, α, α-DIMETHYLBENZYL ETHYL PEROXIDE, AND 1, 2, 3, 4-TETRAHYDRO-1-NAPHTHYL HYDROPEROXIDE

A. A. Balandin, L. Kh. Freidlin, and N. V. Nikiforova

With the aid of recent data on the mean energy of the peroxide bond O – O [1] it was shown by calculation [2] based on the multiplet theory that hydrogenolysis of peroxy compounds should proceed fairly readily over a nickel catalyst. We will here consider this calculation in greater detail.

The hydrogenolysis of an O – O bond is a thermodynamically possible reaction; its course over nickel can be expressed by a doublet scheme:



(1)

If we denote bond energy by Q, then according to the equations of the multiplet theory [3], the heat of formation of the multiplet complex M is in the limit given by

$$E' = -Q_{O-O} + 2Q_{O-Ni} - Q_{H-H} + 2Q_{H-Ni}, \quad (2)$$

since O – O and H – H bonds are broken and the O and H atoms are attracted to nickel (see scheme (1)). Similarly, the heat of decomposition of M is in the limit given by

$$E'' = 2Q_{O-H} - 2(Q_{O-Ni} + Q_{H-Ni}), \quad (3)$$

since two O – H bonds are formed in the reaction products and O and H atoms are torn from the surface.

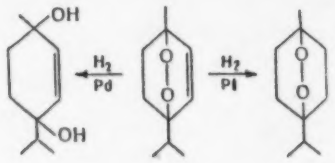
Substituting in Equations (2) and (3) the values of Q known from [2] (see Table 1 in [2]), namely $Q_{O-O} = 47$, $Q_{H-H} = 104.2$, $Q_{O-H} = 110.6$, $Q_{O-Ni} = 48.5$, and $Q_{H-Ni} = 55$ kcal, we find that $E' = 55.8$ and $E'' = 14.2$ kcal/mole. The smaller of the quantities E' and E'', which determines the rate of reaction, is $E'' = 14.2$ kcal/mole. Since E'' is positive, reaction should proceed readily.

According to Cottrell [1], "the determination of the exact value of the heat of formation of organic peroxides meets with great difficulties". The value of Q_{O-O} is therefore not known very accurately. Let

us examine the effect of the possible error in Q_{O-O} on the above result, for which purpose we shall regard Q_{O-O} as a variable in Equations(2)and(3). It will be seen from Equation(3)that E" does not depend on Q_{O-O} because the latter does not occur in the equation. The value of E', which is constant at 14.2 kcal/mole under the given conditions, will determine the rate of reaction until E" becomes equal to E'. Substituting E' = 14.2 and the same values of Q (apart from Q_{O-O}) as before in Equation(2), we find that the limiting value of Q_{O-O} is 88.6 kcal. This limit exceeds the accepted value of 47 kcal by more than 40 kcal, which is certainly very many times the possible experimental error in the determination of Q_{O-O}. Hence, no probable error in the determination of Q_{O-O} can affect our conclusion, namely, that hydrogenolysis of the peroxide bond should proceed readily over nickel.

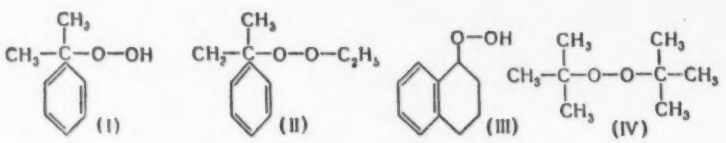
The above calculation concerns the mean O – O bond energy. As we have shown [4], substituents on O must affect E" and the rate of hydrogenolysis. However, until the individual RO – Ni and RO – H bond energies are known in their relation to the nature of the substituent R – as is required for the determination of E" from Equation(3)– such calculations cannot be carried out. The position is just the same for future calculations from Equations(2)and(3)for other catalysts (K), because the C – K, O – K, and H – K bond energies are not yet known. From these examples the importance of determining bond energies concerned in catalytic processes will be seen. At the present only direct experiment can be taken as a basis in such matters.

There has been very little experimental study of the catalytic reduction of organic peroxides. There are only two or three references in the literature to the hydrogenation of peroxy compounds. Paget [5] found that over a palladium catalyst ascaridole is hydrogenated to an unsaturated menthenediol, whereas over a platinum catalyst the double bond is hydrogenated with formation of dihydroascaridole:



Dufraisse and Houpillart [6] showed that in presence of Raney nickel photo-oxides of the anthracene and tetracene series are hydrogenated to the corresponding diols. It is indicated in a patent [7] that the hydrogenation of aromatic hydroperoxides can be effected over Raney nickel and cobalt catalysts under a pressure of 20-25 atm. The corresponding alcohols are obtained; for example, α, α-dimethylbenzyl hydroperoxide (cumene hydroperoxide) gives α, α-dimethylbenzyl alcohol.

There has been no previous investigation into the kinetics of the hydrogenation of peroxides and hydroperoxides. The present paper gives experimental data on the hydrogenation of α, α-dimethylbenzyl hydroperoxide (I), α, α-dimethylbenzyl ethyl peroxide (II), 1, 2, 3, 4-tetrahydro-1-naphthyl hydroperoxide (III), and di-tert-butyl peroxide (IV) over Raney nickel and palladium black.



We obtained data on the rate of hydrogenation of the peroxy group and the effects of various factors on the course of this process. The experiments showed that in presence of Raney nickel the peroxy compounds (I) – (III) are already hydrogenated at 5° under normal pressure. Under these conditions the consumption of hydrogen corresponds to hydrogenation of the peroxide to the alcohol. It was shown by the qualitative reaction with thiocyanate [8] that peroxy compounds were absent from the reaction products.

EXPERIMENTAL

The catalyst was prepared by leaching of 50% Ni-Al alloy powder with 20% sodium hydroxide solution at the boil for two hours. It was washed to neutral reaction (phenolphthalein) and preserved under alcohol.

The solvents used were 96% ethanol, hexyl alcohol, cyclohexane, decahydronaphthalene, and benzene. Hydrogenation was carried out in a hydrogenation flask having a jacket connected to a TS-15 thermostat; the flask, length 180 mm, diameter 35 mm, was placed in a rapid shaker with a length of sweep of 13 cm. The catalyst was introduced into the flask in a stream of hydrogen and saturated with hydrogen for 20 minutes under the same conditions as those used in the experiment (solvent, temperature, rate of agitation). In order to obtain comparable results, each experiment was carried out on a fresh portion of catalyst. The volume of hydrogen was measured every 30 seconds.

The effect of the degree of agitation was studied for the case of α, α-dimethylbenzyl ethyl peroxide. Experiments were carried out at 20° with 0.5 g of Raney nickel and a 0.27-g sample of the peroxide dissolved in 15 ml of ethanol. It was found that with increase in the number of shaking cycles from 500 to 900 per minute the rate of hydrogenation increased slightly, but at above 900 shakes per minute it remains almost constant. The hydrogenation was therefore carried out at 1000 shaking cycles per minute, which ensured that the process occurred in the kinetic region.

Hydrogenation of α, α-Dimethylbenzyl Hydroperoxide. Commercial α, α-dimethylbenzyl hydroperoxide was put through two purification cycles, each consisting in conversion into the sodium salt and decomposition of the salt with 10% sulfuric acid. The hydroperoxide was extracted with benzene, which was then distilled off under reduced pressure. The hydroperoxide had n_D^{20} 1.5230 (the literature [8] gives n_D^{20} 1.5233). The experiments were carried out with 0.3-g portions of hydroperoxide in 15 ml of solvent at 20° in presence of 0.5 g of Raney nickel.

Reaction Order and Effect of Increase in Amount of Catalyst on Reaction Rate. It will be seen from Fig. 1 that the hydrogenation of α, α-dimethylbenzyl hydroperoxide in ethanol in presence of 0.5 g of Raney nickel proceeds at a constant rate, i.e. the reaction is of zero order. This is confirmed by the fact that, with increase in the volume of solvent from 15 to 30 and to 50 ml, the intial rate of absorption of hydrogen in the hydrogenation of 0.3 g of hydroperoxide changed from 14.3 to 14.9 and to 15.4 ml per half-minute. Hence, change in the concentration of the hydroperoxide in the solution does not affect the rate of hydrogenation and the character of the kinetic curve. With increase in the amount of catalyst from 0.5 to 1-1.5 and to 3 g, the rate of reaction changed approximately proportionately (Fig. 1); this indicates that our experiments were carried out in the kinetic region.

Stability of the Catalyst and Effect of the Reaction Products on the Rate of Hydrogenation of the Hydroperoxide. In the course of two or three experiments carried out in succession on a given portion of nickel catalyst (0.5 g), the rate of hydrogenation remained constant. Hence, the catalyst was not deactivated during reaction. Experiments were carried out also in which some reaction product (0.2 g of α, α-dimethylbenzyl alcohol) was added to the hydroperoxide taken for reaction. It will be seen from Fig. 2 that addition of reaction product has no effect on the rate of reduction of α, α-dimethylbenzyl hydroperoxide.

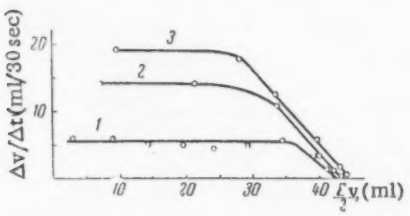


Fig. 1. Effect of increase in catalyst concentration on the rate of hydrogenation of α, α-dimethylbenzyl hydroperoxide: 1) 0.5 g; 2) 1.0 g; 3) 1.5 g.

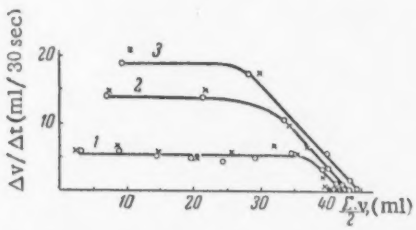


Fig. 2. Effect of reaction products on the rate of hydrogenation of α, α-dimethylbenzyl hydroperoxide: 1) 0.5 g; 2) 1.0 g; 3) 1.5 g (the crosses indicate experiments in which reaction products were added).

Effect of Temperature on Rate of Hydrogenation. The hydrogenation of α, α-dimethylbenzyl hydroperoxide in ethanol in presence of 1.5 g of Raney nickel was carried out at 5, 20, and 30°. The kinetic curves are given in Fig. 3. It will be seen that hydrogenation comes to an end very rapidly – in the course of a few minutes. With rise in temperature the rate of reaction increases. As the process is of zero order, the rate constant of the reaction can be taken as the rate of absorption of hydrogen.

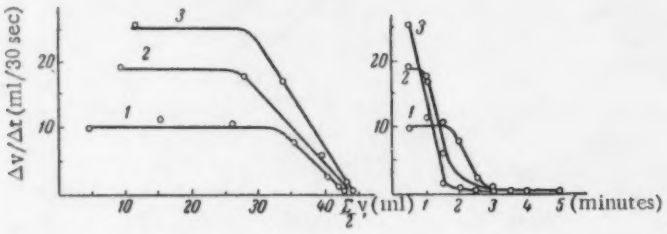


Fig. 3. Effect of temperature on the rate of hydrogenation of α, α-dimethylbenzyl hydroperoxide: 1) 5°; 2) 20°; 3) 30°.

At 5° it is 10 ml per half-minute, at 20° – 19, and at 30° – 25 (Fig. 3). The apparent activation energy ϵ in the range 5-30° calculated from these data is approximately 5 kcal/mole (Fig. 12).

Effect of the Nature of the Solvent on Rate of Hydrogenation. It will be seen from Fig. 4 that the rate of hydrogenation of α, α-dimethylbenzyl hydroperoxide in presence of nickel catalyst (0.5 g) depends on the nature of the solvent. Hydrogenation is most rapid in ethanol, one-half as rapid in hexyl alcohol, and only one-seventh as rapid in cyclohexane and decahydronaphthalene.

Hydrogenation of α, α-Dimethylbenzyl Ethyl Peroxide. The α, α-dimethylbenzyl ethyl peroxide used was pure. The amount of hydrogen consumed in its hydrogenation was that required theoretically. Thus, in the hydrogenation of 0.27 g of the peroxide the volume of hydrogen absorbed (STP) was 33.9, 34.9, and 34.5 ml in triplicate experiments, the theoretical amount being 34.0 ml. All experiments with α, α-dimethylbenzyl ethyl peroxide were carried out with 0.27-g portions in 15 ml of solvent at 20° in presence of 0.5 g of Raney nickel. With increase in volume of solvent from 5 to 30 ml, the initial rate of absorption of hydrogen in the hydrogenation of 0.27 g of the peroxide changed from 6.7 to 6.3 ml per half-minute, i.e. change in the concentration of the peroxide within these limits does not affect the rate of hydrogenation and the character of the kinetic curve.

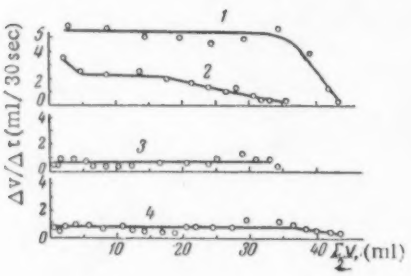


Fig. 4. Effect of the nature of the solvent on the rate of hydrogenation of α, α-dimethylbenzyl hydroperoxide: 1) in ethanol; 2) in hexyl alcohol; 3) in cyclohexane; 4) in decahydronaphthalene.

Reaction Order and Effect of Temperature on Rate of Hydrogenation. It will be seen from Fig. 5 that addition of hydrogen to α, α-dimethylbenzyl ethyl peroxide proceeds with zero-order kinetics as in the case of the hydroperoxide. With rise in temperature the rate of hydrogenation increases, but zero order of reaction is preserved. The apparent activation energy over the temperature range 8-25° is about 5.4 kcal/mole.

Effect of the Reaction Products on the Rate of the Process. Unlike the hydrogenation of the hydroperoxide, the reduction of α, α-dimethylbenzyl ethyl peroxide is retarded appreciably by addition of reaction products (0.2 g) (Fig. 6).

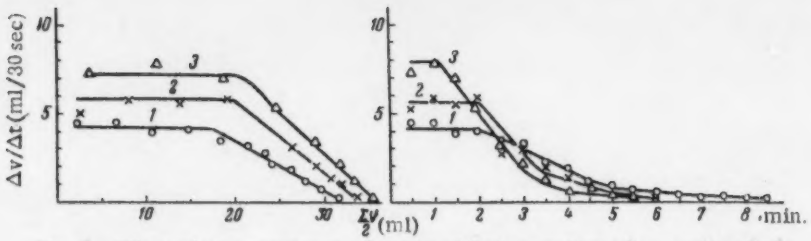


Fig. 5. Effect of temperature on the rate of hydrogenation of α, α-dimethylbenzyl ethyl peroxide: 1) 8°; 2) 15°; 3) 25°.

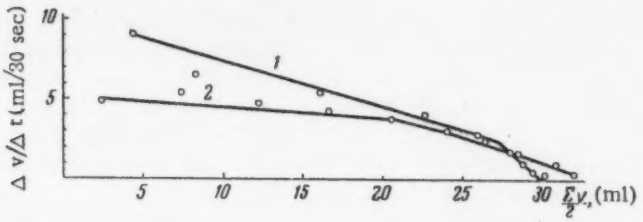


Fig. 6. Effect of reaction products on the rate of hydrogenation of α, α-dimethylbenzyl ethyl peroxide: 1) without addition of reaction products; 2) with addition of reaction products.

Effect of Nature of Solvent. It will be seen from Fig. 7 that the rate of hydrogenation of α, α- dimethylbenzyl ethyl peroxide also depends on the nature of the solvent. Reaction is most rapid in ethanol; it is one-eighth as rapid in cyclohexane, and in decahydronaphthalene and hexyl alcohol the rate of absorption of hydrogen is reduced to one-twelfth.

Hydrogenation in a Thin Film of Alcohol. It was shown previously in our laboratory that olefins dissolved in hydrocarbon solvents are hydrogenated very rapidly in a thin film of alcohol adsorbed beforehand on the surface of the catalyst. We carried out a similar experiment, in which the catalyst was saturated with hydrogen in an alcoholic medium and the hydrogenation was carried out in cyclohexane (after a wash with cyclohexane). It will be seen from Fig. 8 that hydrogenation of the peroxide in cyclohexane over a catalyst saturated with hydrogen in an alcoholic medium proceeds at almost the same rate as in ethanol.

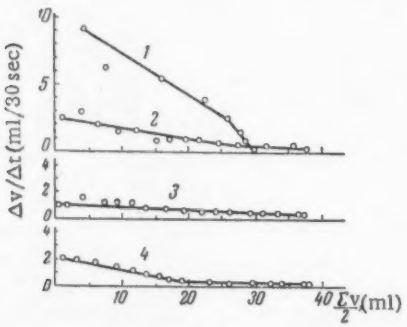


Fig. 7. Effect of the nature of the solvent on the hydrogenation of α, α-dimethylbenzyl ethyl peroxide: 1) in ethanol; 2) in cyclohexane; 3) in hexyl alcohol; 4) in decahydronaphthalene.

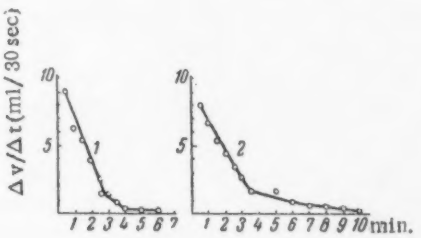


Fig. 8. Hydrogenation of α, α-dimethylbenzyl ethyl peroxide in a thin film of alcohol: 1) in ethanol; 2) in cyclohexane after saturation of catalyst in ethanol.

Hydrogenation of 1, 2, 3, 4-Tetrahydro-1-napthyl Hydroperoxide. The experiments were carried out with 0.15-g portions of the hydroperoxide in 15 ml of solvent at 20° in presence of 0.5 g of Raney nickel.

In successive hydrogenations of 1, 2, 3, 4-tetrahydro-1-naphthyl hydroperoxide over a given portion of Raney nickel, the rate of hydrogenation diminished appreciably on each occasion (Fig. 9), probably owing to oxidation of the catalyst. On the other hand, palladium black (0.1 g) was stable in the reduction of the tetrahydronaphthyl hydroperoxide under the same conditions: in four successive experiments no appreciable reduction in rate of hydrogenation was observed.

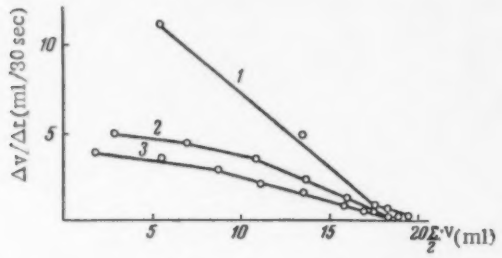


Fig. 9. Deactivation of catalyst in three successive experiments (1-3) on the hydrogenation of 1, 2, 3, 4-tetrahydro-1- naphthyl hydroperoxide.

It follows from Fig. 10 that in presence of Raney nickel the hydrogenation of the tetrahydronaphthyl hydroperoxide in methanol proceeds by a first-order reaction, whereas in benzene the reaction is of zero order; the initial rate of reaction in methanol is about eight times as high as in benzene. It must be pointed out that the rate of reaction in ethanol is generally a little less than in methanol. Over palladium black the reaction is of zero order in both solvents. The nature of the solvent has considerably less effect on reaction rate in presence of palladium black than in presence of Raney nickel (Fig. 11).

Hydrogenation of Di-tert-butyl Peroxide. The preparation used had b.p. 108° and n_D^{20} 1.3908 (the literature [9] gives b.p. 109° and n_D^{20} 1.3910). When di-tert-butyl peroxide (0.37 g) was treated with hydrogen in 15 ml of ethanol at temperatures ranging from 5° to 50° in presence of Raney nickel (0.5 g), no hydrogenation occurred. This confirms statements [9] concerning the exceptional stability of this peroxide in experiments on thermal decomposition (as compared with other peroxides). Its exceptional stability is manifested also, therefore, in the hydrogenation reaction.

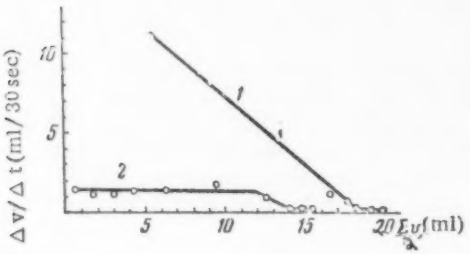


Fig. 10. Rate of hydrogenation of 1, 2, 3, 4-tetrahydro-1-naphthyl hydroperoxide over Raney nickel: 1) in methanol; 2) in benzene.

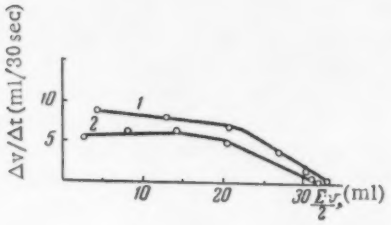


Fig. 11. Rate of hydrogenation of 1, 2, 3, 4-tetrahydro-1-naphthyl hydroperoxide over palladium black: 1) in methanol; 2) in benzene.

The observed rate constants are given in the table, from which it will be seen that the rate constants are affected by the nature and structure of substituents.

By analogy with the kinetics of hydrogenation reactions [10], it must be considered that the constants of zero and first order observed in hydrogenolysis are complex quantities which involve also adsorption coefficients. Activation energies ϵ calculated from these must therefore also be complex quantities and consist in algebraic sums of true activation energies and heats of adsorption. However, the fact that the observed values of ϵ are low (about 5 kcal/mole) is in accord with theoretical calculations, i.e. with the result $E'' > 0$ (see above). This means that the true activation energy must be vanishingly small. As heats of adsorption are low and are to some extent mutually compensating, the observed value of ϵ must be small, which is in accord with experiment (Fig. 12).

TABLE

Peroxy compound	Solvent	Hydrogenation temperature (°C)	Amount of catalyst (g)	Order of reaction	Rate constant (ml/half-min.)	Apparent activation energy (kcal/mole)
α, α-Dimethylbenzyl hydroperoxide	Ethanol	5	1.5	Zero	10	–
		20	1.5	"	19	5.0
		30	1.5	"	25	–
α, α-Dimethylbenzyl ethyl peroxide	Ethanol	8	0.5	"	4.25	–
		15	0.5	"	5.75	5.4
		25	0.5	"	7.25	–
1,2,3,4-Tetrahydro-1-naphthylhydroperoxide	Methanol	20	0.5	First	0.86•	–
	Benzene	20	0.5	Zero	1.3	–
Di-tert-butyl peroxide	Ethanol	5-50	0.5	Not hydrogenated	–	–

• Half-minute^{-1}, since the reaction is of first order.

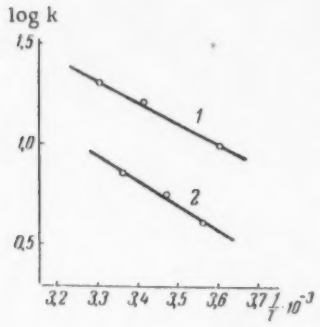


Fig. 12. Activation energy for hydrogenation: 1) α, α-dimethylbenzyl hydroperoxide; 2) α, α-dimethylbenzyl ethyl peroxide.

In conclusion we consider it our pleasant duty to thank K. I. Ivanov, A. P. Meshcheryakov, and B. M. Merkov for the donation of preparations of peroxy compounds.

SUMMARY

1. It was shown that organic peroxides and hydroperoxides are rapidly hydrogenated to the corresponding alcohols over Raney nickel, which is in accord with calculations based on the multiplet theory.

2. The kinetics of these reactions were investigated. It was found that the nature and structure of the substituents affect the rate of reduction, and as a consequence di-tert-butyl peroxide is not hydrogenated at all at temperatures ranging up to 50°.

3. The actions of Raney nickel and palladium catalysts were investigated. The peroxy compounds were hydrogenated over both catalysts, mainly in accordance with a zero-order law. The apparent activation energies for the reduction of peroxides and hydroperoxides were close in value, being 5.4 and 5 kcal/mole respectively. The hydrogenation of α, α-dimethylbenzyl ethyl peroxide was retarded by the reaction products.

4. The rate of catalytic reduction depends on the nature of the solvent. In alcoholic solution reaction proceeds more rapidly than in cyclohexane, benzene, or decahydronaphthalene.

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PREPARATION OF DL-PROLINE AND DL-ORNITHINE FROM 1,1,1,5-TETRACHLOROPENTANE

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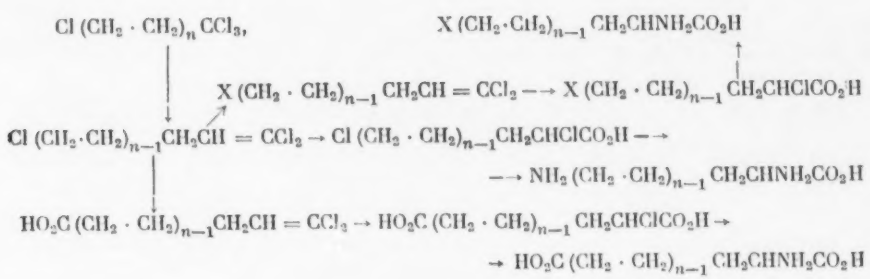
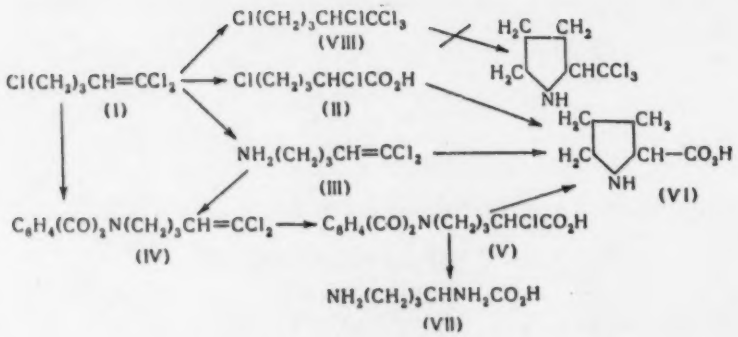
In recent years two of us in collaboration with Zakharkin, Vasilyeva, Petrova, Kost, and Semenov have published• results of investigations on the reactions of α, α, α, ω-tetrachloroalkanes, which have become readily available by the telomerization of ethylene with carbon tetrachloride [2], beginning with the first member of the series, 1, 1, 1, 3-tetrachloropropane, the product of the addition of carbon tetrachloride to ethylene. These workers developed methods for the preparation of ω-amino carboxylic acids from these substances. No less interest was presented by the use of α, α, α, ω-tetrachloroalkanes for the synthesis of α-amino acids, particularly natural amino acids. For this transformation various routes are possible, for example:



It would be expected that, at least in some cases, compounds of the types $Cl(CH_2CH_2)_nCCl_3$, $Cl(CH_2CH_2)_{n-1}CH_2CH=CCl_2$ and $Cl(CH_2CH_2)_{n-1}CH_2CHClCO_2H$, would react through the ω-chlorine with benzene, phenol, indole, and imidazole with formation of homologs of phenylalanine, hydroxyphenylalanine, tryptophan, and histidine. In the present paper we describe the syntheses of DL-proline and DL-ornithine.

According to the literature the best methods of preparing DL-proline [3] and DL-ornithine [4] are those based on acrylonitrile and malonic ester. However, in spite of the high yields obtained in the individual stages, the overall yield of amino acids is comparatively low. We considered that it would be extremely interesting to develop methods for the preparation of these amino acids from the readily accessible 1, 1, 1, 5-tetrachloropentane. Catalytic dehydrochlorination of 1, 1, 1, 5-tetrachloropentane gives 1, 1, 5-trichloro-1-pentene in almost quantitative yield [5]. It appeared that the synthesis of the desired amino acids might be effected in the following ways:

• For a review of these investigations see [1].



Synthesis from 1, 1, 5-trichloro-1-pentene (I) via 5, 5-dichloro-4-pentenylamine (III) was of interest for the solution of the question of the effect of the order of the introduction of the amino groups on the yield of DL-proline, because it ensured that the first amino group entered the 5-position. If cyclization through the 5-amino group proved to be difficult, then this route could be used for the preparation of DL-ornithine. We succeeded in synthesizing DL-ornithine (VII) by the succession of transformations (III) – (V), which include protection of the amino group.

The reaction of 1, 1, 1, 2, 5-pentachloropentane (VIII) is worthy of note. It is known that replacement of chlorine by the action of nucleophilic reagents does not occur in the grouping $-CHCl-CCl_3$. It was of interest to determine whether such replacement can occur under the action of ammonia under conditions which permit intramolecular cyclization.

It is simplest to prepare DL-proline from 1, 1, 1, 5-tetrachloropentane, possibly via 2, 5-dichlorovaleric acid, which is formed in good yield by the conjugated addition of chlorine to 1, 1, 5-trichloro-1-pentene in concentrated sulfuric acid [6]. Gaudry and Berlinquet [7] have described the conversion of 2-bromo-5-chloro-, 2, 5-dibromo-, 2, 5-dichloro-, and 5-bromo-2-chloro-valeric acids into DL-proline by the action of concentrated aqueous ammonia at 70° for 48 hours and at 130° for one hour. The copper salt of DL-proline was obtained in yields of 40, 25, 25, and 10% respectively.

We made a detailed study of the action of ammonia on 2, 5-dichlorovaleric acid with variation of temperature, duration of reaction, concentration of ammonia, and the extent of its excess, and in presence and absence of ammonium carbonate. The results are given in Table 1.

Workers have usually separated DL-proline from ammonium chloride with the aid of its silver salt and purified it by conversion into the copper salt. There is a reference to the preparation of DL-proline from its hydrochloride with the aid of the anion-exchange agent Amberlite or treatment with a tertiary amine, but in both cases unsatisfactory results were obtained [3]. We separated DL-proline and ammonium chloride with the aid of cation-exchange resins [8], an acetic acid solution of isatin being used as a qualitative reagent for DL-proline. This method is simple and permits complete separation of DL-proline and ammonium chloride.

As will be seen from Table 1, the yield of DL-proline in experiments with liquid ammonia did not exceed 25% and when the reaction was carried out at a higher temperature the yield fell (Experiments 1-3). When the reaction was carried out with a 25% solution of ammonia in alcohol, both at room temperature and at 150°, the yield of DL-proline remained low (Table 1, Experiments 4 and 5). It was of interest to study the behavior of 2, 5-dichlorovaleric acid toward ammonia in presence of ammonium carbonate. Experiments were carried out with various relative amounts of reactants at room temperature and 40-50° with subsequent decomposition of ammonium carbonate at 80-100°. The yield of DL-proline then attained 30% (Table 1, Experiments 6 and 7).

The best results were obtained by the reaction of 2, 5-dichlorovaleric acid with 25% aqueous ammonia at 20-35° for 72 hours, which gave a 50-53% yield of DL-proline (Table 1, Experiment 9). It was shown that reduction in the duration of reaction to 14 hours had almost no effect on the yield of DL-proline (Table 1, Experiments 10 and 11).

TABLE 1

Experiment	Amount of 2,5-dichlorovaleric acid (g)	Ammonia concentration	Amount of ammonia (ml)	Amount of ammonia (moles/mole of acid)	Duration of reaction (hours)	Temperature (°C)	Yield of DL-proline (%)	Method of isolation of DL-proline
1	15	Liquid	125	63	3	100	13.7	Cu salt
2	15	"	125	63	3	70	17.3	Cu salt
3	15	"	125	63	72	25	25.0	Cu salt
4	15	25% alcoholic	300	50	72	25	5	
5	14.7	Ditto	300	50	2.5	140—150	9.3	Cu salt
6*	17.1	25% aqueous	75	12	10	40—45	27.2	Cu salt
7*	17.1	"	75	12	48	25	17.9	Condensation product with isatin
8	10	"	175	43	1	130	27.0	Cu salt
9	15	"	350	58	72	20—35	53.9	Cu salt and free proline
10	15	"	350	58	24	30—35	50.0	Cu salt
11	12.5	"	280	58	14	30—35	49.5	Cu salt
12**	15.0	"	280	58	24	30—35	51.3	Free proline + Cu salt
13**	15	"	280	58	24	30—35	53.7	Cu salt

* The experiments were carried out in presence of ammonium carbonate (8 moles per mole of 2, 5-dichlorovaleric acid).

** The experiments were carried out with 2-bromo-5-chlorovaleric acid.

The ammonolysis of 2-bromo-5-chlorovaleric acid under the optimum conditions for the preparation of DL-proline from 2, 5-dichlorovaleric acid gave a 51-54% yield of DL-proline (Table 1, Experiments 12 and 13). Hence, under our conditions there is no advantage in using 2-bromo-5-chlorovaleric acid for the preparation of DL-proline.

In view of the exceptional accessibility of 1, 1, 1, 5-tetrachloropentane and the high yields obtained in the synthesis of the intermediaries 1, 1, 5-trichloro-1-pentene and 2, 5-dichlorovaleric acid, this method of synthesizing DL-proline must be regarded as the simplest and most convenient at the present time.

By the action of alcoholic ammonia on ethyl 2, 5-dichlorovalerate at 130-140° and hydrolysis of the intermediate product with boiling concentrated hydrochloric acid, DL-proline was obtained in 31% yield.

We carried out the conjugated addition of chlorine to 5, 5-dichloro-4-pentenylamine in concentrated sulfuric acid at 0-5°. In view of the mild conditions under which we carried out this reaction, we hoped that in this way we should obtain 5-amino-2-chlorovaleric acid or its cyclization product. Investigation of the reaction showed that the main product was DL-proline, isolated in 41% yield in the form of its copper salt. In addition we obtained 5-amino-2-chlorovaleric acid and 4, 5, 5, 5-tetrachloropentylamine in low yields. We must emphasize the extreme readiness with which the intermediately formed 5-amino-2-chlorovaleric acid undergoes cyclization. Owing to this fact this route cannot be used for the preparation of DL-ornithine. Hence, for the preparation of DL-ornithine we started from 2-chloro-5-phthalimidovaleric acid prepared by the conjugated addition of chlorine in sulfuric acid to N-(5, 5-dichloro-4-pentenyl) phthalimide, a reaction which proceeds very smoothly with a high yield of the acid. Ammonolysis of 2-chloro-5-phthalimidovaleric acid with 25% aqueous ammonia (in absence and in presence of ammonium carbonate, in the cold and at higher temperatures) gave a mixture of DL-ornithine and DL-proline (Table 2). Ornithine was isolated as the monohydrochloride and was characterized as DL-ornithuric acid. In some experiments the yield of proline was determined by preparing its condensation product with isatin. The best yield of DL-ornithine was obtained by reaction in presence of ammonium carbonate at 100° (31-33%). The simultaneous yield of DL-proline was 21-30% (Table 2, Experiments 1 and 4). It is probable that DL-proline was formed by removal of the phthaloyl

group from 2-chloro-5-phthalimidovaleric acid under ammonolysis conditions, since the reaction mixture after ammonolysis gave a positive reaction with isatin.

TABLE 2

Experiment	Amount of				Temperature (°C)	Duration of reaction (hours)	Yield (%) of	
	2-chloro-5-phthalimidovaleric acid (g)	25% ammonia (ml)	Ammonium carbonate (g)	Ammonia (moles/mole of acid)			DL-ornithine monohydrochloride	DL-proline
1	10	35	45	80	100	4	20	21.5
2	10	35	45	80	45–55	12	23	–
3	6	25	27	80	100	15	31.4	30.0
4	30	125	135	80	100	15	33.0	21.2
5	5	120	–	350	30	14	10.0	–
6	5	120	–	350	100	4	18.2	–

The action of ammonia on 1, 1, 1, 2, 5-pentachloropentane in an alcohol medium resulted in the smooth formation of 4, 5, 5-trichloro-4-pentenylamine hydrochloride. This indicates that chlorine in the α-position to a CCl_3 group is incapable of taking part in intramolecular substitution. Reaction of 1, 1, 1, 2, 5-pentachloropentane with the potassium derivative of phthalimide went analogously, the product being N-(4, 5, 5-trichloro-4-pentenyl) phthalimide.

EXPERIMENTAL

Action of Ammonia on 2, 5-Dichlorovaleric Acid. A solution of 15 g of 2, 5-dichlorovaleric acid in 350 ml of 25% aqueous ammonia was set aside at 20-35° for 72 hours. Ammonia was removed on a water bath and the solution was passed through a column of Cationite CDB, in which the amino acid was absorbed. The cation-exchange resin was washed with distilled water until the reaction for chloride was negative, and proline was then eluted with 5% ammonia. This process was controlled by means of the reaction with isatin, which gives a blue coloration and precipitate with proline in an acetic acid medium. The eluate was evaporated down and gave a slightly colored solid residue, from which proline was extracted with alcohol and reprecipitated with dioxane; weight 6.5 g. Recrystallization from absolute alcohol gave 2.55 g (25.5%) of proline, m.p. 202-203° (the literature gives 203° [9], 205° [10], and 210-211° [3]).

Found %: C 52.43; 52.42; H 7.99; 8.06; N 12.18; 12.24 $C_5H_9O_2N$. Calculated %: C 52.17; H 7.83; N 12.12

The alcoholic filtrate was evaporated to dryness, 10 g of copper carbonate in water was added to the residue, and the mixture was heated in a water bath. Concentration of the aqueous solution gave 4.1 g of the copper salt of proline (28.4% yield).

Found %: N 8.12; 8.24; Cu 19.01; 19.12 $C_{10}H_{20}O_6N_2Cu$. Calculated %: N 8.52; Cu 19.38

Heating of DL-proline with picric acid in aqueous solution gave proline picrate, m.p. 135-136° (from water); the literature [7] gives m.p. 135-137°.

Found %: C 38.20; 38.13; H 3.50; 3.49; N 16.46; 16.37 $C_{11}H_{12}N_4O_9$. Calculated %: C 38.37; H 3.48; N 16.28

The total yield of DL-proline was 53.9% on the amount of 2, 5-dichlorovaleric acid taken.

Action of Ammonia on 2-Bromo-5-chlorovaleric Acid. A solution of 15 g of 2-bromo-5-chlorovaleric acid in 280 ml of 25% ammonia was set aside at 20-30° for 48 hours. The reaction mixture was treated as

described above. Recrystallization from absolute alcohol gave 0.8 g (10%) of proline, m.p. 201-202°. Precipitation of the alcoholic filtrate with dioxane gave a further 4 g of proline, m.p. 176-183°, which was converted into the copper salt by heating it with copper carbonate in water. The weight of copper salt of proline was 4.7 g (41.3%). The total yield of proline was 51.5% on the amount of 2-bromo-5-chlorovaleric acid taken.

Action of Ammonia on Ethyl 2, 5-Dichlorovalerate in Alcohol. A mixture of 30 g of ethyl 2, 5-dichlorovalerate and 16.5 g of ammonia in 90 ml of alcohol was heated in an autoclave for three hours at 130°. The precipitate of ammonium chloride was filtered off and washed with alcohol. The residue remaining after removal of alcohol was heated for a few hours with concentrated hydrochloric acid. The resulting solution was evaporated under reduced pressure with addition of water for the more complete removal of hydrochloric acid. The resulting oil was heated with a solution of isatin in acetic acid and gave 15.2 g of the condensation product of proline and isatin [11]. The yield was 31% on the amount of ethyl 2, 5-dichlorovalerate taken.

4, 5, 5-Trichloro-4-pentenylamine. A mixture of 12.3 g of 1, 1, 1, 2, 5-pentachloropentane and 24 g of ammonia in 150 ml of ethanol was heated at 100° for three hours. After removal of alcohol the reaction mixture was treated with dilute hydrochloric acid. The undissolved residue, 4, 5, 5-trichloro-4-pentenylamine hydrochloride, was washed several times with water and dried; weight 4.5 g (41.6%).

Found %: C 27.20; 27.07; H 4.23; 4.27 $C_5H_9Cl_4N$. Calculated %: C 26.66; H 4.00

The hydrochloric acid solution was made alkaline and extracted with ether. Solvent was distilled off, and vacuum distillation of the residue gave 3.8 g (40%) of 4, 5, 5-trichloro-4-pentenylamine, b.p. 70-71° (5 mm); n_D^{20} 1.5120; d_4^{20} 1.3180; Found MR 42.92; Calculated MR 42.85.

Found %: C 31.96; 31.97; H 4.41; 4.39 $C_5H_8Cl_3N$. Calculated %: C 31.33; H 4.12

N-(4, 5, 5,-Trichloro-4-pentenyl) phthalimide. A mixture of 12 g of 1, 1, 1, 2, 5-pentachloropentane, 23 g of the potassium derivative of phthalimide, and 25 ml of absolute ethanol was heated for six hours at 185-190°. The precipitate was filtered off, washed with alcohol, and treated with benzene in the cold. The substance obtained from the benzene was N-(4, 5, 5-trichloro-4-pentenyl)phthalimide, m.p. 87-88° (from alcohol). The yield was 10.2 g (61.3%).

Found %: C 48.80; 48.69; H 3.11; 3.17; N 4.75; 4.69 $C_{13}H_{10}O_2Cl_3N$. Calculated %: C 48.52; H 3.11; N 4.48

Action of Chlorine on 5, 5-Dichloro-4-pentenylamine in Concentrated Sulfuric Acid. Chlorine was passed through a stirred,cooled (with snow) solution of 12.5 g of 5, 5-dichloro-4-pentenylamine in 30 ml of concentrated sulfuric acid until hydrogen chloride was no longer liberated. The reaction mixture was poured slowly into 40 ml of water, and 25% aqueous ammonia was then added until the reaction was neutral. The copious precipitate was filtered off and washed with water, when most of it dissolved. The weight of undissolved precipitate (1) was 0.75 g. The substance was 4, 5, 5, 5-tetrachloropentylamine hydrochloride. It gave a ninhydrin reaction in a weakly alkaline medium, and it contained halogen; m.p. (with decomposition) 195-197° (from water).

Found %: C 21.58; 21.60; H 3.68; 3.77; Cl 68.17; 67.07; N 5.18; 5.16 $C_5H_{10}Cl_5N$. Calculated %: C 22.90; H 3.81; Cl 68.00; N 5.36

When allowed to stand, the aqueous filtrate gave a crystalline precipitate (2), weight 0.5 g. This gave a positive ninhydrin reaction and contained halogen. Its properties and analysis indicated that it was 5-amino-2-chlorovaleric acid, m.p. 138°.

Found %: C 39.41; 39.37; H 6.66; 6.54; Cl 23.78; 23.15 $C_5H_{12}O_2ClN$. Calculated %: C 39.60; H 6.60; Cl 23.40

The filtrate from precipitates (1) and (2) was diluted to 800 ml with water and passed through a column of KU-2 cation-exchange resin. The amino acid was eluted with the aid of 5% aqueous ammonia. The ammoniacal eluate was vacuum-evaporated to dryness. The substance obtained gave a positive reaction for proline with isatin. It was dissolved in water and heated with copper carbonate. After being recrystallized from water, the resulting copper salt of proline amounted to 5.5 g (41.5% on the amount of 5, 5-dichloro-4-pentenylamine taken).

Found %: N 8.52; 8.66 $C_{10}H_{20}O_6N_2Cu$. Calculated %: N 8.54

Preparation of N-(5, 5-Dichloro-4-pentenyl)phthalimide. a) From 5, 5-dichloro-4-pentenylamine. A mixture of 4.3 g of 5, 5-dichloro-4-pentenylamine and 5 g of phthalic anhydride was heated at the melting point in an oil bath for several hours. The melt was heated with alcohol. When cool the solution gave 6 g (75%) of glistening crystals of N-(5, 5-dichloro-4-pentenyl)phthalimide, m.p. 106-107°. It was shown to be identical to the N-(5, 5-dichloro-4-pentenyl)phthalimide prepared from 1, 1, 5-trichloro-1-pentene (see next experiment).

b) From 1, 1, 5-trichloro-1-pentene. A mixture of 70 g of the potassium derivative of phthalimide, 65 g of 1, 1, 5-trichloro-1-pentene, and 20 ml of absolute ethanol was heated in an autoclave at 185-195° for 12 hours. The reaction mixture was treated first with petroleum ether to remove 1, 1, 5-trichloro-1-pentene and then with benzene in the cold. Evaporation of the benzene filtrate to dryness gave 80 g of N-(5, 5-dichloro-4-pentenyl)phthalimide, m.p. 102-103°, raised to 107° by recrystallization from alcohol. The yield was 75% on the amount of 1, 1, 5-trichloro-1-pentene taken.

Found %: C 55.08; 55.07; H 3.95; 3.95; Cl 24.88; 25.17; N 5.19; 5.28 $C_{13}H_{11}NCl_2O_2$.
Calculated %: C 54.93; H 3.87; Cl 25.00; N 4.93

Approximately the same results were obtained by carrying out the reaction in excess of 1, 1, 5-trichloro-1-pentene in absence of alcohol.

Preparation of 2-Chloro-5-phthalimidovaleric Acid. N-(5, 5-Dichloro-4-pentenyl)phthalimide (9 g) was added to 40 ml of concentrated sulfuric acid, and the solution was cooled with snow and stirred vigorously while a stream of chlorine was passed. At the beginning of the reaction there was a vigorous evolution of hydrogen chloride, and this practically ceased after three hours. The solution was gradually poured into cooled water (60 ml). The thick oil that was precipitated rapidly solidified. The precipitate was ground and washed repeatedly with water until the acid reaction to Congo red disappeared. The weight of dry product, m.p. 114.5-115°, was 8.2 g (92%). After recrystallization from benzene the 2-chloro-5-phthalimidovaleric acid melted at 118-119°. The literature [12] gives m.p. 109-112°.

Found %: C 55.31; 55.19; H 4.40; 4.31; Cl 13.17; 12.58 $C_{13}H_{12}O_4NCl$. Calculated %:
C 55.41; H 4.26; Cl 12.61

Action of Ammonia on 2-Chloro-5-phthalimidovaleric Acid. Ammonium carbonate (135 g) in 45 ml of water was added to 30 g of 2-chloro-5-phthalimidovaleric acid in 125 ml of 25% aqueous ammonia. The reaction mixture was heated at 100° in a shaking autoclave for 15 hours. The reaction mixture was heated for one hour on a water bath and then evaporated to dryness under reduced pressure. Concentrated hydrochloric acid was added to the residue, and the solution was heated in a boiling water bath for 12 hours. After dilution with water, the phthalic acid that separated was filtered off. Residual phthalic acid was extracted from the filtrate with ether, and the filtrate was evaporated to dryness under reduced pressure, the operation being repeated with the addition of water for the more complete removal of hydrochloric acid. Alcohol was added to the dry residue, the precipitate of ammonium chloride was filtered off, and concentrated ammonia was added to the filtrate to pH 6-7. The precipitate (1) of DL-ornithine monohydrochloride was filtered off and heated with two 150-ml portions of alcohol to remove ammonium chloride. The weight of DL-ornithine monohydrochloride was 5.9 g (33%).

Benzoylation of the DL-ornithine with benzoyl chloride in an alkaline medium gave DL-ornithuric acid,

m.p. 186-187° (from alcohol); the literature [13] gives m.p. 186-187°.

Found %: C 66.65; 66.85; H 5.79; 5.90; N 8.32; 8.38 $C_{19}H_{20}N_2O_4$. Calculated %: C 67.06; H 5.88; N 8.23

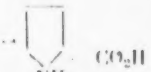
The alcoholic filtrate from the precipitate (1) was concentrated under reduced pressure, and a solution of 10 g of isatin in acetic acid was added to the residue. The reaction mixture was heated in a water bath for one hour. The dark-green precipitate formed was filtered off, washed, first with acetic acid and then several times with water, and boiled twice with alcohol to remove isatin. The weight of condensation product of DL-proline with isatin was 7.4 g (21.2%).

SUMMARY

1. DL-Proline was prepared by several routes from 1, 1, 1, 5-tetrachloropentane.

It was shown that the best of these routes to the preparation of DL-proline is the following:

$$Cl(CH_2)_3CH_2CCl_3 \rightarrow Cl(CH_2)_3CH=CCl_2 \rightarrow Cl(CH_2)_3CHClCO_2H \rightarrow$$



2. DL-Ornithine was prepared from 1, 1, 5-trichloro-1-pentene in the following way:

$$Cl(CH_2)_3CH=CCl_2 \rightarrow C_6H_4(CO)_2N(CH_2)_3CH=CCl_2 \rightarrow$$
$$\rightarrow C_6H_4(CO)_2N(CH_2)_3CHCl-CO_2H \rightarrow NH_2(CH_2)_3CHNH_2CO_2H.$$

3. It was shown that, under the action of ammonia or the potassium derivative of phthalimide, 1, 1, 1, 2, 5-pentachloropentane is converted into 4, 5, 5-trichloro- -pentenylamine or N-(4, 5, 5-trichloro-4-pentenyl)phthalimide, respectively. No replacement of the chlorine atom in the α-position to the CCl_3 group occurs.

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SYNTHESIS AND POLYMERIZATION OF ORGANOSILICON COMPOUNDS CONTAINING A METHACRYLOYL GROUP

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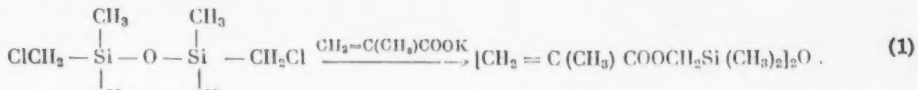
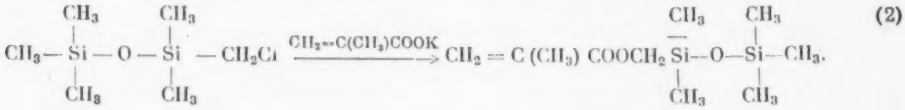
There are references in the literature [1-7] to the preparation of polymers from organosilicon compounds containing a double bond in a silicon-attached hydrocarbon radical. The alkenylhalo- and alkenylalkoxysilanes which have been described contain allyl, 2-methylallyl, and vinyl groups, which are of low activity in polymerization reactions. As a result, resins from these compounds must be prepared at high temperatures for long periods, which must limit their application in industry. The replacement of the allyl or vinyl group of the organosilicon compound by a functional group containing an active double bond (e.g. methacryloyl or acryloyl) makes it possible to obtain compounds that polymerize rapidly at moderate temperatures.

In the present paper we describe the preparation and polymerization of some new organosilicon compounds: 1,3-bis (methacryloyloxymethyl)tetramethyldisiloxane, (methacryloyloxymethyl)pentamethyldisiloxane, and triethoxy(methacryloyloxymethyl)silane. These compounds were obtained by reaction of 1,3-bischloromethyltetramethyldisiloxane, (chloromethyl)pentamethyldisiloxane, and (chloromethyl)triethoxysilane with potassium methacrylate in an autoclave at 180° in presence of a copper catalyst and hydroquinone as inhibitor.

The reactions were as follows:



(1)



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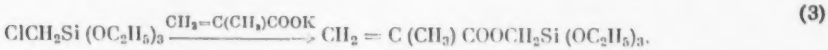


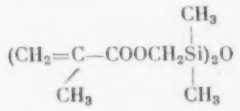
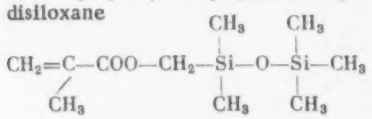
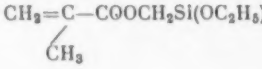
(3)

The compounds obtained (for properties see Table 1) are colorless liquids of faint characteristic odor which are able to polymerize at moderate temperatures with formation of clear, solid, glasslike polymers. The processes of polymerization of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane and (methacryloyloxymethyl) pentamethyldisiloxane to the gelation stage at 65° in presence of 0.1-0.5% of benzoyl peroxide are represented in Figures 1 and 2.

The experimental data in Figures 1 and 2 on the kinetics of the polymerization of organosilicon compounds containing a methacryloyloxy group attached to carbon in the α-position to silicon show that for these compounds in presence of peroxy initiators the polymerization process is of the same type as in the case of ordinary organic compounds containing methacryloyl groups.

The compounds obtained were able not only to polymerize at moderate temperatures, but also to copolymerize with acrylic and methacrylic esters and with styrene. The processes of copolymerization of

TABLE 1

Name and formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR	
				Found	Calculated
1. 1,3-Bis(methacryloyloxymethyl)tetramethyldisiloxane 	134—135 (2)	1.4450	1.0022	87.69	88.56
2. (Methacryloyloxymethyl)pentamethyldisiloxane 	73—74 (4)	1.4200	0.9100	68.31	68.74
3. Triethoxy(methacryloyloxymethyl)silane 	99—100 (3)	1.4220	1.0181	65.79	66.27

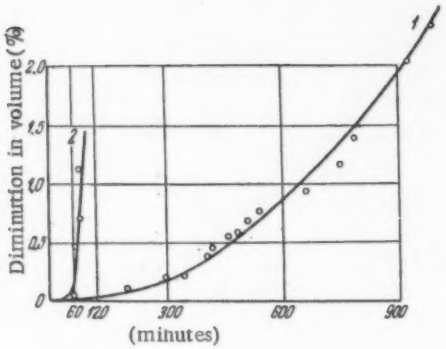


Fig. 1. Relation between rate of polymerization of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane and amount of initiator: 1) 0.1% Bz_2O_2; 2) 0.5% Bz_2O_2.

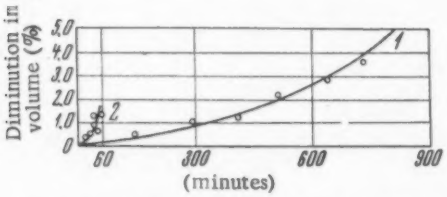


Fig. 2. Relation between rate of polymerization of (methacryloyloxymethyl)pentamethyldisiloxane and amount of initiator: 1) 0.1% Bz_2O_2; 2) 0.5% Bz_2O_2.

1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane (25-75% by weight) with the methyl and butyl esters of acrylic and methacrylic acids (75-25% by weight) and with styrene (75-25% by weight) and of (methacryloyloxymethyl)pentamethyldisiloxane (25-75% by weight) with methyl methacrylate (75-25% by weight) in presence of 0.1% of benzoyl peroxide at 65° are represented graphically in Figs. 3-8. From these experimental data it follows (see Curves 1 and 3, Figs. 3-6) that the relative rate of copolymerization of mixtures containing given amounts of the methyl and butyl esters of acrylic and methacrylic acids increases as we pass from butyl esters to methyl esters, which is probably determined by the differing rates of polymerization of these esters.

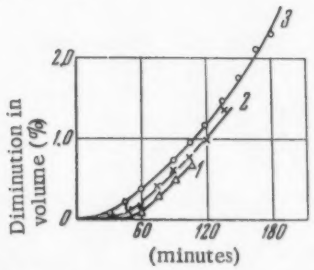


Fig. 3. Relation between rate of copolymerization of 1,3,-bis(methacryloyloxymethyl)tetramethyldisiloxane with methyl acrylate (MA) and composition: 1) 25% MA; 2) 50% MA; 3) 75% MA

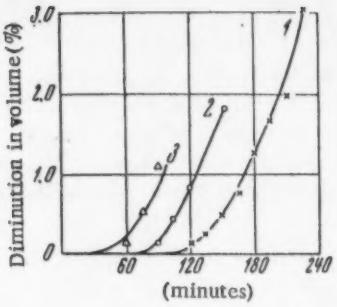


Fig. 4. Relation between rate of copolymerization of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane with butyl acrylate (BA) and composition: 1) 75% BA; 2) 50% BA; 3) 25% BA.

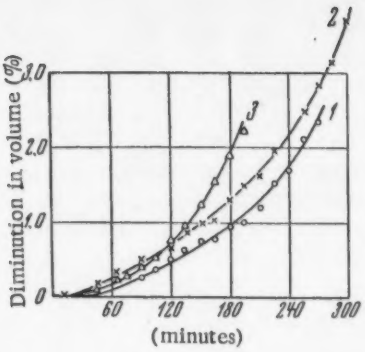


Fig. 5. Relation between rate of copolymerization of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane with methyl methacrylate (MMA) and composition: 1) 75% MMA; 2) 50% MMA; 3) 25% MMA.

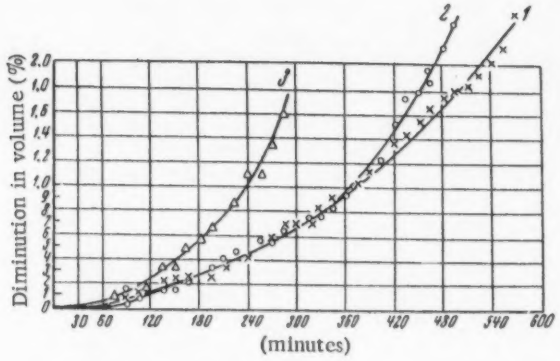


Fig. 6. Relation between rate of copolymerization of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane with butyl methacrylate (BMA) and composition: 1) 75% BMA; 2) 50% BMA; 3) 25% BMA.

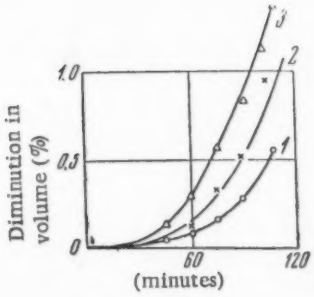


Fig. 7. Relation between rate of copolymerization of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane with styrene and composition: 1) 75% of styrene; 2) 50% of styrene; 3) 25% of styrene.

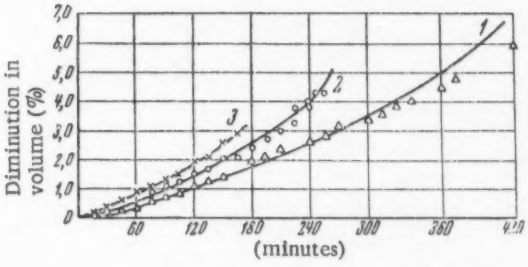


Fig. 8. Relation between rate of copolymerization of (methacryloyloxymethyl)pentamethyldisiloxane with methyl methacrylate (MMA) and composition: 1) 25% MMA; 2) 50% MMA; 3) 75% MMA.

The mixtures containing (methacryloyloxymethyl)pentamethyldisiloxane and methyl methacrylate, 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane and methyl and butyl acrylates, the same disiloxane and styrene, the same disiloxane and 50-75% by weight of methyl methacrylate, and the same disiloxane and 50-25% by weight of butyl methacrylate set to clear glasslike products. As a result of the copolymerization of 75% by weight of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane with 25% by weight of methyl methacrylate and of the same disiloxane (25% by weight) with 75% by weight of butyl methacrylate we obtained heterogeneous products (absence of complete transparency). It is probable that copolymerization of these monomers in these particular proportions is accompanied by partial homopolymerization, which determines the peculiar courses of Curves 3 and 1 of Figs. 5 and 6. All the glasslike copolymers obtained had thermal stabilities that did not surpass that of polymethyl methacrylate.

Investigation of the solubility of products obtained from compositions containing 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane showed that they contained 95-98% of insoluble copolymers in all the examples cited – for acrylic and methacrylic esters and also for styrene. Hence, the copolymerization process proceeds almost to the limit for all these compositions.

Hence, heating in presence of peroxy initiators of organosilicon compounds containing a methacryloyloxy group on a carbon in the α-position to silicon with acrylic and methacrylic esters and with styrene at weight ratios varying from 25 to 75% results mainly in copolymerization.

EXPERIMENTAL

Synthesis of Monomers

For the synthesis of organosilicon monomers containing a methacryloyl group we used: 1,3-bischloromethyltetramethyldisiloxane (n_D^{20} 1.4390 and d_{20}^{20} 1.041), obtained by the hydrolysis of chloro(chloromethyl)dimethylsilane; (chloromethyl)pentamethyldisiloxane (n_D^{20} 1.4105 and d_{20}^{20} 0.9150), obtained by the cohydrolysis of chloro(chloromethyl)dimethylsilane and chlorotrimethylsilane; (chloromethyl)triethoxysilane (n_D^{20} 1.4010 and d_{20}^{20} 1.085), obtained by reaction of trichloro(chloromethyl)silane with alcohol.

1. 1,3-Bis(methacryloyloxymethyl)tetramethyldisiloxane. A mixture of 173 g (0.75 mole) of 1,3-bischloromethyltetramethyldisiloxane, 223 g (1.8 moles) of potassium methacrylate, 108 ml (6 moles) of water, 10 g of hydroquinone, and 20 g of copper turnings was heated with agitation in an autoclave for five hours at 180°. The cooled reaction mixture was diluted with water until the precipitated salt dissolved. The product was separated with the aid of a separating funnel, dissolved in ether, washed with water until test for chloride ($AgNO_3$) was negative, and dried over calcined sodium sulfate. Fractionation gave 28 g (0.10 mole) of unchanged bischloromethyltetramethyldisiloxane, b.p. 82-83° (18 mm) and 121 g of 1,3-bis(methacryloyloxymethyl)tetramethyldisiloxane (for properties see Table 1). With allowance for reactant recovered unchanged the yield was 56%.

Found %: C 50.5; H 7.93; Si 16.73 $C_{14}H_{26}O_5Si_2$. Calculated %: C 50.9; H 7.88; Si 16.97

2. (Methacryloyloxymethyl)pentamethyldisiloxane. A mixture of 39.2 g (0.2 mole) of (chloromethyl)pentamethyldisiloxane, 34.5 g (0.28 mole) of potassium methacrylate, 15 ml (0.8 mole) of water, 2 g of hydroquinone, and 4 g of copper was heated in an autoclave with agitation for five hours at 200°. The procedure described above gave a 15.2% yield of (methacryloyloxymethyl)pentamethyldisiloxane (for properties see Table 1).

Found %: C 48.4; H 8.77; Si 22.60 $C_{10}H_{22}O_3Si_2$. Calculated %: C 48.8; H 8.94; Si 22.75

3. Triethoxy(methacryloyloxymethyl)silane. A mixture of 42.4 g (0.2 mole) of (chloromethyl)triethoxysilane, 34.5 g (0.28 mole) of potassium methacrylate, 17 ml (0.3 mole) of absolute ethanol, 2 g of hydroquinone, and 4 g of copper was heated with agitation in an autoclave for eight hours at 180°. The reaction mixture was cooled, and precipitated salt was filtered off. Vacuum fractionation gave 15 g of triethoxy(methacryloyloxymethyl)silane (for properties see Table 1) and 6 g of unchanged (chloromethyl)triethoxysilane, b.p. 90-91° (25 mm). With allowance for reactant recovered unchanged the yield was 34%.

Found %:* Si 10.57; ethoxy groups 53.23 $C_{11}H_{22}O_5Si$. Calculated %: C 50.04; H 8.78; Si 10.68; ethoxy groups 51.62

Study of the Mass Polymerization of the Synthesized Monomers and their Mass Copolymerization with Methacrylic and Acrylic Esters and with Styrene

Our study of the mass polymerization of the synthesized monomers and their mass copolymerization with acrylic and methacrylic esters and with styrene consisted in the determination of comparative rates of polymerization and copolymerization and the yields of the polymers and copolymers formed. The comparative rate of polymerization was determined by the dilatometric method, which enables one to follow the course of polymerization from the diminution in volume up to the point at which the whole of the ester is converted into gel. The monomers, washed free from hydroquinone and containing 0.1-0.5% of benzoyl peroxide, were poured into 5-ml ampoules calibrated accurately within 0.01 ml. The ampoules were sealed and placed in a thermostat regulated to 65 ± 0.2°. The reduction in the volume occupied by the ester was read every 15 minutes until gelation occurred.

TABLE 2

No.	Composition of initial mixture (%)		Taken (g)	Ether extraction		Acetone extraction		Am. of insoluble copolymer (%)
	*	Second monomer		Loss (g)	Am. of monomer (%)	Loss (g)	Am. of polymer (%)	
		Methyl acrylate						
1	25	75	2.0140	0.0760	3.75	0.0080	0.40	95.85
2	50	50	1.1702	0.0450	3.85	0.0035	0.30	96.85
3	75	25	1.2010	0.0354	2.95	0.0072	0.60	96.45
		Butyl acrylate						
4	25	75	2.0086	0.0515	2.60	0.0140	0.70	96.70
5	50	50	1.1360	0.0250	2.27	0.0056	0.50	97.33
6	75	25	1.1768	0.0200	1.69	0.0037	0.32	98.00
		Methyl methacrylate						
7	25	75	1.0888	0.0098	0.40	0.0200	1.86	97.74
8	50	50	1.3345	0.0127	0.95	0.0270	2.05	97.00
9	75	25	1.0883	0.0460	4.25	0.0102	0.93	95.92
		Butyl methacrylate						
10	25	75	1.0806	0.0057	0.48	0.0435	4.02	95.50
11	50	50	2.1513	0.0340	1.58	0.0027	1.21	97.31
12	75	25	1.9208	0.0500	2.63	0.0021	1.13	96.24
		Styrene						
13	25	75	1.8807	0.0172	2.05	0.0094	0.50	97.45
14	50	50	1.8192	0.0425	2.35	0.0150	0.82	96.83
15	75	25	1.6596	0.0530	3.20	0.0151	0.91	95.89

* 1,3-Bis(methacryloyloxymethyl)tetramethyldisiloxane.

For the determination of yields of polymers and copolymers the ampoules were heated for 50 hours at 65°. The polymers were then removed, ground, and weighed, and a 1-2 g sample was placed in a Soxhlet and ether-extracted for 24 hours in order to determine the monomer content. The sample was dried to constant weight and acetone-extracted for 24 hours, after which it was dried and weighed. The experimental results obtained are given in Table 2.

* We were unable to determine C, H, and Si by elementary analysis, apparently owing to the formation of silicon carbide.

SUMMARY

1. The following new organosilicon compounds were synthesized: a) 1,3-bis(methacryloyloxymethyl) tetramethyldisiloxane; b) (methacryloyloxymethyl)pentamethyldisiloxane; and c) triethoxy(methacryloyloxymethyl)silane.

2. It was shown that these compounds readily polymerize at 65° in presence of benzoyl peroxide.

3. It was shown that these compounds are able to copolymerize with acrylic and methacrylic esters and with styrene at 65° in presence of benzoyl peroxide with formation of transparent solids.

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REACTIONS OF 3,3,3-TRICHLOROPROPENE AND 1,1,1,3-TETRACHLOROPROPANE WITH AROMATIC AMINES

R. Kh. Freidlina and N. A. Semenov

As we showed in a previous paper [1], in the reactions of 3,3,3-trichloropropene and of 1,1,3-trichloropropene with chlorobenzene, with bromobenzene, and with anisole in presence of aluminum chloride, smooth substitution of the group $CH_2CH = CCl_2$ occurs in the benzene ring, mainly in the para position:

$$XC_6H_5 + \begin{cases} CH_2 = CH - CCl_3; \\ CH_2Cl - CH = CCl_2 \end{cases} \xrightarrow{AlCl_3} p\text{-}XC_6H_4CH_2CH = CCl_2 + HCl,$$

in which

$$X = Cl,\ Br,\ CH_3O.$$

With phenol, both in presence and in absence of aluminum chloride, a mixture of ortho and para derivatives is obtained on heating, but with alkaline aqueous sodium phenoxide, not only ortho and para C-alkylation occurs, but also O-oxidation with formation altogether of three substances:

$$C_6H_5OH + \begin{cases} CH_2 = CH = CCl_3 \\ CH_2Cl - CH = CCl_2 \end{cases} \xrightarrow{NaOH} \begin{cases} p\text{-}HOC_6H_4CH_2CH = CCl_2 \\ o\text{-}HOC_6H_4CH_2CH = CCl_2 \\ C_6H_5OCH_2CH = CCl_2. \end{cases}$$

In the present investigation we studied the reactions of 3,3,3-trichloropropene with aniline, N-methylaniline, and N,N-dimethylaniline in absence of catalysts and also the reactions of the first two aromatic amines with 1,1,1,3-tetrachloropropane. On analogy with phenol [1] and diethylamine [2], in the reactions of aniline and N-methylaniline with 3,3,3-trichloropropene we might expect both N- and C-alkylation to occur. Actually, under the conditions studied only N-alkylation products were obtained. Thus, in the reaction of 3,3,3-trichloropropene with aniline a good yield was obtained of N-(3,3-dichloroallyl)aniline, the structure of which was proved by its conversion into the hydrochloride of N-phenyl-β-alanine ether ester and determination of the melting point of this in admixture with the hydrochloride obtained by reaction of aniline with ethyl 3-chloropropionate. A low yield was obtained also of a product containing two 3,3-dichloroallyl groups per molecule of aniline and probably having the tertiary amine structure $C_6H_5N(CH_2CH = CCl_2)_2$. This structure is in accord with the fact that the substance cannot be acylated and can be prepared in high yield by heating the above mentioned N-(3,3-dichloroallyl)aniline with excess of 3,3,3- or 1,1,3-trichloropropene, the reaction being analogous with the reactions of the same trichloropropenes with N-methylaniline. N-methyl- and N,N-dimethyl-anilines gave the same substance, $C_6H_5N(CH_3)CH_2CH = CCl_2$.

This structure is the only one possible, since in the case of alkylation of the aromatic ring two different substances would be obtained. Reaction with N,N-dimethylaniline was accompanied by elimination of methyl chloride, probably from the intermediately formed quaternary ammonium compound $[C_6H_5N(CH_3)_2CH_2CH{=}CCl_2]Cl$.

In all the cases studied, 1,1,3-trichloropropene ($CH_2CH-CH=CCl_2$) reacts with aromatic amines just like 3,3,3-trichloropropene. It has been noted on several occasions that 1,1,1,3-tetrachloropropane differs from higher $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes in that the lone chlorine cannot be replaced by other atoms or groups by the action of nucleophilic reagents [3, 4]. In the reactions of 1,1,1,3-tetrachloropropane with aniline and N-methylaniline, we succeeded in obtaining in low yield and identifying in the form of hydrochlorides two compounds of the following structures: $C_6H_5NHCH_2CH_2CCl_3$ and $C_6H_5N(CH_3)CH_2CH_2CCl_3$. The structure of the first of these was proved by the following transformations

$$C_6H_5NHCH_2CH_2CCl_3 \rightarrow C_6H_5N(COCH_3)CH_2CH_2CCl_3 \rightarrow C_6H_5N(COCH_3)CH_2CH=CCl_2 \rightarrow$$
$$\rightarrow C_6H_5N(COCH_3)CH_2CH_2COOH$$

and determination of the melting point of a mixture of the final product with a known sample of N-acetyl-N-phenyl-β-alanine. The structure of the second compound was proved by its conversion by treatment with sodium ethoxide into $C_6H_5N(CH_3)CH_2CH=CCl_2$, conversion of this into its hydrochloride, and determination of the melting point of a mixture of the product and an authentic sample of the hydrochloride.

EXPERIMENTAL

Reaction of 3,3,3-Trichloropropene with Aniline. A mixture of 75 g of $CCl_3CH=CH_2$ and 325 g of freshly distilled aniline was boiled for one hour, treated with saturated sodium carbonate solution, cooled, and extracted with ether. The ether extracts were dried over calcined sodium sulfate. After removal of solvent and excess of aniline (under reduced pressure), the residue was fractionated.

Fraction I, amounting to 81 g (77%), had b.p. 122-123° (4 mm), n_D^{20} 1.5873; d_4^{20} 1.2522. It was a colorless liquid which smelled like aniline. As will be shown below, it was N-(3,3-dichloroallyl) aniline $C_6H_5NHCH_2CH=CCl_2$.

Found %: C 53.74; 53.72; H 4.52; 4.57 $C_9H_9Cl_2N$. Calculated %: C 53.49; H 4.49

Its hydrochloride (from concentrated hydrochloric acid or alcohol-ether mixture) had m.p. 144-145°.

Found %: C 45.32; 45.10; H 4.24; 4.25 $C_9H_{10}Cl_3N$. Calculated %: C 45.31; H 4.23

Fraction II, amounting to 5 g (5%), had b.p. 156-157° (3.5 mm), n_D^{20} 1.5945; d_4^{20} 1.3516.

Found %: C 46.61; 46.63; H 3.62; 3.67 $C_{12}H_{11}Cl_4N$. Calculated %: C 46.34; H 3.57

The chemical behavior of Fraction II corresponded to that of the tertiary base $C_6H_5N(CH_2CH=CCl_2)_2$, the hydrochloride of which has m.p. 139-140° (from benzene). The same base was obtained in 65% yield by heating N-(3,3-dichloroallyl) aniline with excess of 1,1,3-trichloropropene. The identity of the two hydrochlorides was proved by a mixture melting point test.

Found %: Cl 51.07; 51.15 $C_{12}H_{12}Cl_5N$. Calculated %: Cl 51.02

N-Phenyl-β-alanine Ethyl Ester. A mixture of 30.3 g of $C_6H_5NHCH_2CH=CCl_2$, prepared as described above, and 120 g of 94% H_2SO_4 was heated with stirring for one hour at 120-145°. After about 95% of the calculated amount of hydrogen chloride had been liberated, 60 ml of ethanol was added gradually to the hot reaction mixture, after which the solution was heated for a further 20 minutes at 80-90°. The cooled reaction mixture was added carefully to a concentrated aqueous solution of sodium carbonate and extracted with ether or chloroform. Solvent was distilled off, and vacuum-distillation of the residue gave 23 g (80%) of N-phenyl-β-alanine ethyl ester, b.p. 146-147° (8 mm), n_D^{20} 1.5313; d_{20}^{20} 1.0679. The melting point of the hydrochloride was 98-99° (from ethanol-ether). The literature [5] gives b.p. 185-186° (30 mm), n_D^{20} 1.5315; d_{20}^{20} 1.0709 for the free amino ester and m.p. 98-99° for the hydrochloride. The hydrochloride obtained gave no depression of

melting point in admixture with the hydrochloride of N-phenyl-β-alanine ethyl ester synthesized directly from aniline and ethyl 3-chloropropionate.

Preparation of N-Acetyl-N-phenyl-β-alanine. a) A solution of 15 g of $C_6H_5NHCH_2CH = CCl_2$ in 30 g of acetic anhydride was boiled for one hour. Excess of acetic anhydride was distilled off, and distillation of the residue under reduced pressure gave an acylated product of structure $C_6H_5N(COCH_3)CH_2CH = CCl_2$, a colorless oil, b.p. 138-139° (4 mm), n_D^{20} 1.5550; d_4^{20} 1.2399.

Found %: C 54.57; 54.40; H 4.78; 4.65 $C_{11}H_{11}OCl_2N$. Calculated %: C 54.12; H 4.55

The same product is obtained in quantitative yield by the action of acetic anhydride on the hydrochloride of the base. b) A vigorously stirred mixture of 15.8 g of $C_6H_5N(COCH_3)CH_2CH = CCl_2$ and 50 g of 94% H_2SO_4 was heated for one hour at 100° and for a further 30 minutes at 110°. After the liberation of almost the calculated amount of hydrogen chloride, the reaction mixture was poured onto ice and, if no crystals were precipitated immediately, extracted with chloroform. The chloroform was distilled off, and the residue was recrystallized from hot water and gave 12.1 g (90%) of colorless crystals (m.p. 110-111°).

Found %: C 63.84; 63.97; H 6.32; 6.31; N 6.52; 6.89 $C_{11}H_{13}O_3N$. Calculated %: C 63.75; H 6.32; N 6.76

Reaction of 3,3,3-Trichloropropene with N-Methylaniline. A mixture of 3,3,3-trichloropropene and 107 g of N-methylaniline was refluxed for one hour. Saturated sodium carbonate solution was added to the hot mixture until gas evolution ceased; the mixture was then cooled and extracted with chloroform. Solvent and excess of N-methylaniline (under reduced pressure) were distilled off. Distillation of the residue gave 35 g (76%) of $C_6H_5N(CH_3)CH_2CH = CCl_2$, b.p. 120° (5 mm) and 135° (9 mm), n_D^{20} 1.5800; d_4^{20} 1.2142;.

Found %: C 55.49; 55.70; H 5.22; 5.21; Cl 32.76; 32.93 $C_{10}H_{11}Cl_2N$. Calculated %: C 55.56; H 5.13; Cl 32.81

The hydrochloride, obtained by saturation of an ether solution of the base with hydrogen chloride, had m.p. 126° after recrystallization from dry toluene.

Found %: C 47.26; 47.05; H 4.75; 4.70 $C_{10}H_{12}Cl_3N$. Calculated %: C 47.55; H 4.79

Reaction of 3,3,3-Trichloropropene with N,N-Dimethylaniline. A mixture of 58 g (0.4 mole) of $CCl_3CH = CH_2$ and 240 g of N,N-dimethylaniline was refluxed for four hours. The weight of the reaction mixture fell by 20 g, which is equivalent to a loss of almost 0.4 mole of methyl chloride. Excess of N,N-dimethylaniline was distilled off, and distillation of the residue in a stream of nitrogen under reduced pressure gave 73 g (85%) of a colorless substance of b.p. 119-120° (5 mm), n_D^{20} 1.5800; d_4^{20} 1.2144, identical with the substance obtained in the reaction with N-methylaniline (b.p. 120° (5 mm); n_D^{20} 1.5800; d_4^{20} 1.2142). The hydrochloride was prepared by saturation of an ether solution of this base with hydrogen chloride. After recrystallization from dry toluene it had m.p. 126°, undepressed by admixture of the hydrochloride described above (previous experiment). The same base in equally high yields was obtained by reaction of N-methyl- and N,N-dimethyl-anilines with 1,1,3-trichloropropene.

Reaction of 1,1,1,3-Tetrachloropropane with Aniline. a) A mixture of 112 g of $CCl_3CH_2CH_2Cl$ and 281 g of freshly distilled aniline was refluxed for two hours. The solution was cooled, aniline hydrochloride was filtered off, and unchanged tetrachloropropane was distilled off in steam. The organic layer was separated from water and was distilled under reduced pressure in order to remove aniline as completely as possible. The residue was washed three times with hot water to remove traces of hydrochloride. Distillation under a reduced pressure of nitrogen gave a fraction (20 g) having b.p. 127-128° (3 mm), n_D^{20} 1.5765; d_4^{20} 1.3182. This substance was a faintly yellowish liquid which decomposed violently in attempts to distill it with zinc dust. When

it was warmed with sodium ethoxide, NaCl was precipitated and $C_6H_5NHCH_2CH = CCl_2$ was formed, this product being completely identical with that obtained by reaction of 1,1,3-trichloropropene or 3,3,3-trichloropropene with aniline.

Owing to the small difference in boiling point between the substances $C_6H_5NHCH_2CH = CCl_2$ and $C_6H_5NHCH_2CH_2CCl_3$ and the thermal instability of the latter, it was fairly difficult to isolate the base $C_6H_5NHCH_2CH_2CCl_3$ from the mixture in the pure state; it was therefore identified as the hydrochloride, which was prepared by saturating an ether solution of the base with hydrogen chloride. Ether was evaporated off, and the residue was treated with hot benzene, in which the hydrochloride $C_6H_5NHCH_2CH = CCl_2 \cdot HCl$ is fairly soluble. The hydrochloride $C_6H_5NHCH_2CH_2CCl_3 \cdot HCl$ was recrystallized from ethanol: colorless crystals, m.p. 170-171°.

Found %: C 39.28; 39.47; H 4.15; 4.16 $C_9H_{11}Cl_4N$. Calculated %: C 39.30; H 4.03

b) Acylation. The hydrochloride $C_6H_5NHCH_2CH_2CCl_3 \cdot HCl$ (8.62 g) was dissolved in 30-35 ml of acetic anhydride, acetic anhydride was then distilled from the mixture under reduced pressure at 80-90°, and the residue was vacuum-distilled. An almost quantitative yield of a colorless viscous substance, b.p. 154° (3 mm), n_D^{20} 1.5460; d_4^{20} 1.3054, was obtained. It solidified after a short time: m.p. 47° (from petroleum ether).

Found %: C 46.97; 46.80; H 4.10; 4.11 $C_{11}H_{12}OCl_3N$. Calculated %: C 47.08; H 4.31

c) Dehydrochlorination and hydrolysis. The acylated product (6.5 g) was treated with an equimolecular amount of sodium ethoxide in 15 ml of ethanol. The mixture was heated, precipitated sodium chloride was filtered off, and the filtrate was diluted with water. The oil that separated was extracted with ether, ether was distilled off, and vacuum distillation of the residue gave 5 g of a colorless substance identical in constants with the acetyl derivative of N-(3,3-dichloroallyl)aniline prepared from aniline and 3,3,3-trichloropropene. Hydrolysis of this substance with five times its weight of concentrated sulfuric acid at 100-120° gave colorless crystals, m.p. 110-110.5° (from hot water). There was no depression of melting point in a mixture test with the N-acetyl-N-phenyl-β-alanine prepared previously.

Reaction of 1,1,1,3-Tetrachloropropane with N-Methylaniline. Reaction of 36 g of 1,1,1,3-tetrachloropropane and 44 g of N-methylaniline was carried out as described for tetrachloropropane and aniline. Vacuum fractionation of the product gave a fraction of b.p. 125-135° (5 mm), n_D^{20} 1.5720; d_4^{20} 1.2393. Repeated recrystallization from benzene of the hydrochloride prepared from this base gave a substance melting with decomposition at 178-179°.

Found %: C 41.90; 42.00; H 4.51; 4.53 $C_{10}H_{13}Cl_4N$. Calculated %: C 41.55; H 4.53

Treatment of this hydrochloride with sodium ethoxide gave a base havinga hydrochloride of m.p. 126°, undepressed by admixture of the hydrochloride obtained from N-methylaniline and 3,3,3-trichloropropene.

SUMMARY

1. The reactions of 3,3,3-trichloropropene and 1,1,3-trichloropropene with aniline, N-methylaniline, and N,N-dimethylaniline were studied, and it was shown that with these trichloropropenes aniline gives the substance $C_6H_5NHCH_2CH = CCl_2$ and N-methyl- and N,N-dimethyl-anilines both give $C_6H_5N(CH_3)CH_2CH{=}CCl_2$.

2. By the formation of the hydrochlorides $C_6H_5NHCH_2CH_2CCl_3 \cdot HCl$ and $C_6H_5N(CH_3)CH_2CH_2CCl_3 \cdot HCl$ in the reaction of 1,1,1,3-tetrachloropropane with aniline and N-methylaniline, respectively, it was shown that the lone chlorine in 1,1,1,3-tetrachloropropane can undergo nucleophilic substitution. Unlike reactions of nucleophilic reagents with higher α,α,α,ω-tetrachloroalkanes, these reactions give low yields.

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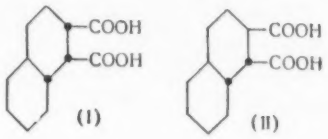
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 18. SYNTHESIS OF TRANS-SYN-CIS-DECAHYDRO-1,2,-NAPHTHALENEDICARBOXYLIC ACID

I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

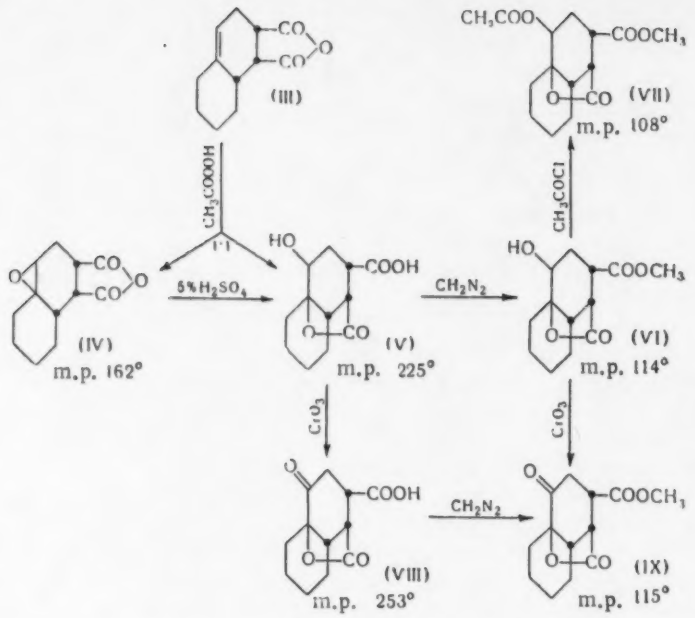
As a result of a detailed study of the stereochemistry of the diene-synthesis reaction between 1-vinylcyclohexene and maleic anhydride and the stereospecific transformations of the isomeric adducts formed, we obtained six of the eight theoretically possible geometric isomers of decahydro-1,2-naphthalenedicarboxylic acid [1], the configurations of which were proved rigorously. The other two isomers of this acid, having trans-syn-cis (I) and trans-syn-trans (II) configurations, could not be obtained by these methods; we did not succeed also in preparing them by the condensation of 1-(1-acetoxyvinyl)cyclohexane with maleic anhydride owing to the fact that this reaction proceeds in the direction contrary to that required by the rule of "maximum accumulation of unsaturation" [2] and gives an adduct of anti configuration.



(I) (II)

However, an examination of molecular models showed that trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I) should be quite stable, and its synthesis was very important for the confirmation of all the previously established steric laws. As will be seen from the configuration of this acid, in order to prepare it we had to find a route which would lead to a trans ring fusion with simultaneous preservation of the cis disposition of hydrogens at C-1, C-2, and C-8a. We succeeded in finding such a synthesis by studying the oxidation of the previously prepared anhydride of syn-cis-1, 2, 3, 5, 6, 7, 8, 8a-octahydro-1,2-naphthalenedicarboxylic acid (III) [3] with peroxyacetic acid.

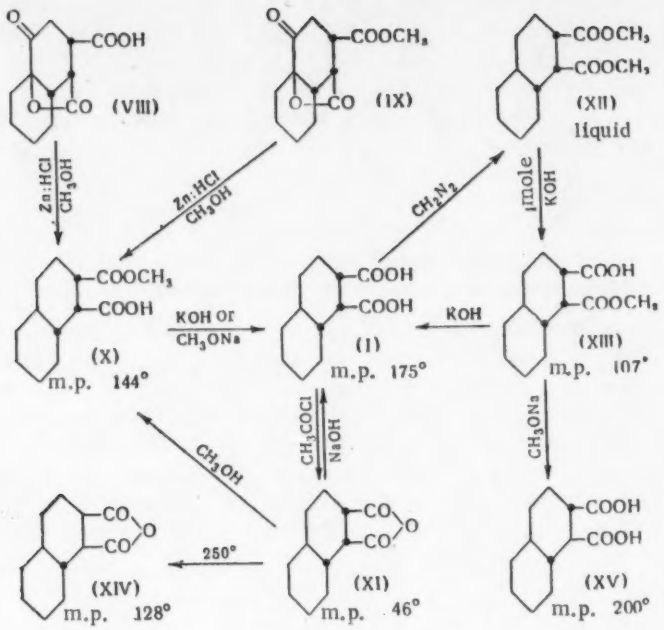
It was found that reaction of the syn-cis anhydride (III) with peroxyacetic acid in chloroform gave a good yield of a mixture of approximately equal amounts of the corresponding epoxide (IV) and the syn-cis 4-hydroxy γ-lactone acid (V), the latter being readily formed also by the hydrolysis of the epoxide (IV) with 5% sulfuric acid. The structure of the syn-cis 4-hydroxy γ-lactone acid (V) was proved by the fact that diazomethane converted it into the syn-cis 4-hydroxy γ-lactone ester (VI) which has a carbonyl absorption band in the infrared spectrum at 5.6 μ, characteristic for the γ-lactone ring. The presence of a secondary hydroxy group was confirmed by the formation of the corresponding acetic ester (VII) by boiling the hydroxy ester (VI) with acetyl chloride. The configuration of the 4-hydroxy γ-lactone acid (V) at C-1, C-2, C-4a, and C-8a follows quite obviously from the syn-cis configuration of the original anhydride (III) and the cis reaction of lactonization of the anhydride (IV) with participation of the axial carboxyl at C-1 and the epoxy ring. However, the configuration of the hydroxy group at C-4 is still not proved.



Oxidation of the syn-cis 4-hydroxy γ-lactone acid (V) with chromium trioxide in acetic acid gave a good yield of the syn-cis 4-oxo γ-lactone acid (VIII), which was converted by diazomethane into the corresponding oxo lactone ester (IX), formed also by the oxidation of the syn-cis 4-hydroxy γ-lactone ester (VI). Thus, quite apart from the configuration of the epoxy ring and the 4-hydroxy group in the intermediaries (IV) and (V), we obtained the 4-oxo γ-lactone ester (VIII) and its ester (IX) with cis dispositions of the hydrogens at C-1, C-2, and C-8a which could serve as starting materials for a possible synthesis of trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I).

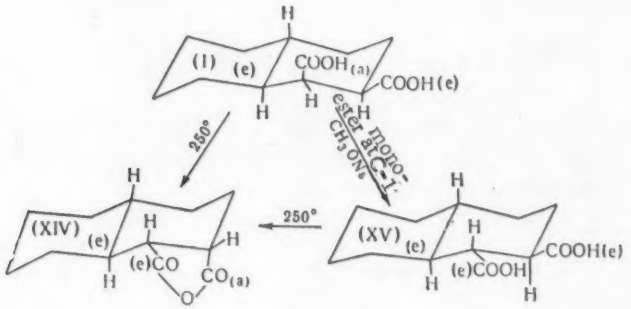
For the preparation of this compound we made use of Clemmensen reduction of the oxo lactones (VIII) and (IX) because we might then expect that, in addition to removal of the oxo group, hydrogenolysis of the γ-lactone ring would occur with preservation of the original configuration. Similar reduction of a lactone ring has been observed recently in the catalytic hydrogenation of some simple oxo lactones [4], but this reaction has not been studied at all for polycyclic compounds. It was found that boiling of the syn-cis 4-oxo γ-lactone acid (VIII) with amalgamated zinc in a mixture of concentrated hydrochloric acid and methanol resulted in the reduction of the oxo group, esterification of the 2-carboxyl, and hydrogenolysis of the γ-lactone ring, the trans-syn-cis monoester (X) being obtained in good yield. The structure of this compound was proved unequivocally by the fact that it is formed also by similar reduction of the syn-cis 4-oxo γ-lactone ester (IX). Such hydrogenolysis of the γ-lactone ring occurs readily only in the case of oxo lactones, and the previously described lactones of decahydro-1,2-naphthalenedicarboxylic acid [5], which contain no oxo group, and the above-described 4-hydroxy γ-lactone acid were found to be incapable of such hydrogenolysis.

The configuration of the monoester (X) follows from the syn-cis configuration of the original 4-oxo γ-lactone acid (VIII) and the cis reaction of hydrogenolysis of the γ-lactone ring. This last circumstance does not give rise to doubt, since in this case Walden inversion at C-4a is impossible without conversion of a trans-decahydronaphthalene system into a cis-decahydronaphthalene system, which has never been observed to occur. In accordance with its structure and configuration, the monoester (X) should not undergo isomerization at the equatorial (stable) 2-methoxycarbonyl group and therefore should give by hydrolysis the expected trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I), differing from the previously described six other isomers; this was confirmed experimentally.



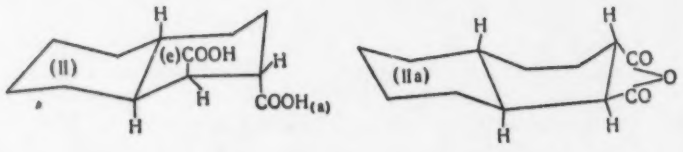
It was found that the monoester (X), both when hydrolyzed with aqueous alkali and when boiled with alcoholic sodium methoxide, gave the same trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I), which differed from the previously described stereoisomers and which formed the corresponding trans-syn-cis anhydride (XI) and diester (XII). The latter was readily hydrolyzed by 1 mole of aqueous-alcoholic alkali at the less screened 2-methoxycarbonyl group with formation of the trans-syn-cis monoester (XIII) in which the 1-carboxyl is esterified, whereas boiling of the trans-syn-cis anhydride (XI) with methanol gave the above-described isomeric monoester (X).

The trans-syn-cis configuration of the acid (I) and its assignment to the trans-decahydronaphthalene series were confirmed by a study of the transformations of the corresponding anhydride (XI) and monoester (XIII). It was found that, in accordance with previously established laws, the trans-syn-cis anhydride (XI) is isomerized when heated to 250° into the more stable trans-anti-cis anhydride (XIV), identical with the product obtained previously [3]. In a similar way, by isomerization at the axial 1-methoxycarbonyl group, the trans-syn-cis monoester (XIII) gave the previously described trans-anti-trans-decahydro-1,2-naphthalenedicarboxylic acid (XV) [1]. It is not difficult to see that such transformations are possible only when the acid (I) has a trans-syn-cis configuration, which follows also from the method by which it was prepared.



All the above-described transformations of trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I) are completely in accord with molecular models, from which it will be seen that, owing to the rigidity of the trans-decahydronaphthalene system, the isomerization of the trans-syn-cis acid (I) can proceed only at the axial (unstable) 1-carboxyl so that the monoester (XIII) is readily converted into trans-anti-trans-decahydro-1,2-naphthalenedicarboxylic acid (XV), which has two stable equatorial carboxyls. As similar isomerizations occur at esterified carboxyls, the isomeric monoester (X) with an equatorial 2-carboxyl should not be capable of undergoing isomerization when treated with sodium methoxide, which is in fact found to be so. As in all previously described analogous cases, the thermal isomerization of the trans-syn-cis acid (I) gives the more stable system of the trans-anti-cis anhydride (XIV), in which the carbon-carbon bonds at C-1 and C-8a have the more energetically favorable diequatorial arrangement, there is an equatorial-axial arrangement of these bonds at C-2 and C-8a, and the five-membered anhydride ring has the cis configuration.

Hence, seven of the eight theoretically possible geometric isomers of decahydro-1,2-naphthalenedicarboxylic acid have now been prepared, and their configurations have been proved by stereospecific transformations and independent syntheses. Four of these isomers are in the cis-decahydronaphthalene series, and the other three have the trans arrangement of the rings. However, we have not succeeded in preparing the eighth isomer predicted by theory and having the trans-syn-trans configuration (II). As can be seen from an examination of molecular models, this eighth isomer, trans-syn-trans-decahydro-1,2-naphthalenedicarboxylic acid(II) should be of low stability, since in the form of the free acid it can exist only with a diaxial arrangement of carboxy groups and in the form of the anhydride (IIa) it will have the energetically unfavorable "bathlike" structure of the B ring.



The fact that, in spite of all the work that we have done, we have not obtained this unstable trans-syn-trans acid (II) confirms the correctness of the configuration of all the other seven isomers of decahydro-1,2-naphthalenedicarboxylic acid and of the steric laws on which the proof of these configurations was based.

EXPERIMENTAL*

Oxidation of the Anhydride of syn-cis-1, 2, 3, 5, 6, 7, 8, 8a-Octahydro-1,2-naphthalenedicarboxylic Acid (III)

Peroxyacetic acid (90% 3 ml) was added slowly to a stirred solution of 7 g of the syn-cis anhydride (III) [3] in 25 ml of dry chloroform at 20-25°, and the mixture was left at room temperature for four hours. The crystalline precipitate was filtered off and washed with ether, the product being 1.5 g of the epoxide (IV), m.p. 161-162°. The mother liquor was evaporated, the liquid residue was treated with ether, and the precipitate formed was filtered off and carefully washed with ether. In this way we obtained a further 2.7 g of the same epoxide, m.p. 161-162°. Recrystallization from benzene did not affect the melting point.

Found %: C 64.73; 64.83; H 6.29; 6.33 $C_{12}H_{14}O_4$. Calculated %: C 64.85; H 6.30

The ethereal mother liquor was evaporated, and the liquid residue was dissolved by warming it slightly with 30 ml of 5% sodium hydroxide solution. The solution was acidified with sulfuric acid and allowed to stand overnight. A precipitate (2.3 g) of the syn-cis 4-hydroxy γ-lactone acid (V), m.p. 215-217°, formed. After recrystallization from acetone it had a constant melting point of 224-225°.

Found %: C 60.29; 60.10; H 6.88; 6.78 $C_{12}H_{16}O_5$. Calculated %: C 60.00; H 6.71

* All melting points are corrected.

syn-cis 4-Hydroxy γ-Lactone Acid (V)

The epoxide (IV) (0.5 g) was dissolved by warming it slightly with 4 ml of 5% sodium hydroxide solution, 3 ml of 10% sulfuric acid was added, and the mixture was boiled for three hours. On cooling an oil was precipitated; it solidified overnight. Crystallization from a mixture of acetone and benzene gave 0.2 g of the syn-cis 4-hydroxy γ-lactone acid (V), m.p. 220-222°, undepressed by admixture of the sample obtained previously (above).

syn-cis 4-Hydroxy γ-Lactone Ester (VI)

A suspension of 0.7 g of the syn-cis 4-hydroxy γ-lactone acid (V) in ether was treated with ethereal diazomethane. Ether was distilled off, and crystallization of the residue from benzene gave 0.55 g of pure syn-cis 4-hydroxy γ-lactone ester (VI), melting constantly at 113-114°.

Found %: C 61.50; 61.68; H 7.03; 7.21 $C_{13}H_{18}O_5$. Calculated %: C 61.40; H 7.13

For this ester the infrared spectrum in carbon tetrachloride solution was determined; it had carbonyl absorption bands characteristic for the methoxycarbonyl group (1735 cm^{-1}) and the γ-lactone ring (1783 cm^{-1}).

syn-cis 4-Acetoxy γ-Lactone Ester (VII)

A mixture of 0.9 g of the syn-cis 4-hydroxy γ-lactone ester (VI) and 10 ml of acetyl chloride was boiled for one hour, and volatile substances were distilled off under reduced pressure. The liquid residue was caused to crystallize by treatment with petroleum ether. Recrystallization from diethyl ether gave 0.75 g of pure syn-cis 4-acetoxy γ-lactone ester (VII), m.p. 107-108°.

Found %: C 60.82; 60.97; H 6.75; 6.78 $C_{15}H_{20}O_6$. Calculated %: C 60.79; H 6.80

syn-cis 4-Oxo γ-Lactone Acid (VIII)

A solution of 3.7 g of chromium trioxide in 200 ml of acetic acid and 5 ml of water was added over a period of six hours to a stirred solution of 9.7 g of the syn-cis 4-hydroxy γ-lactone acid (V) in 300 ml of acetic acid. The product was left overnight at room temperature, excess of chromium trioxide was removed by addition of methanol, and the solution was evaporated to low bulk under reduced pressure. The precipitate that formed was filtered off and washed on the filter with a little acetic acid and then with ether. The product (7.1 g) was the syn-cis 4-oxo γ-lactone acid (VIII), m.p. 248-250°. After crystallization from 80% aqueous acetone, pure (VIII) was obtained in the form of fine glistening needles, melting with decomposition at 252-253°.

Found %: C 60.42; 60.39; H 5.95; 5.86 $C_{12}H_{14}O_5$. Calculated %: C 60.49; H 5.92

Titration with alkali showed that the product contained only one free carboxy group.

syn-cis 4-Oxo γ-Lactone Ester (IX)

a) A solution of 1.8 g of the syn-cis 4-hydroxy γ-lactone ester (VI) in acetic acid was treated as before with 0.6 g of chromium trioxide, the excess of which was removed by addition of methanol. The solution was evaporated to dryness under reduced pressure, and the solid residue was extracted with 100 ml of boiling benzene. The extract was washed with sodium bicarbonate solution and dried over sodium sulfate. Benzene was distilled off, and the crystalline oxidation product was washed on a filter with a little ether. The product (1.35 g) was the syn-cis 4-oxo γ-lactone ester (IX), m.p. 112-114°, raised to 114-115° by crystallization from 1 : 3 benzene-ether. There was considerable depression of melting point in admixture with the original hydroxy ester (VI).

Found %: C 62.00; 61.94; H 6.41; 6.47 $C_{13}H_{16}O_5$. Calculated %: C 61.89; H 6.39

b) A suspension of 1 g of the syn-cis 4-oxo γ-lactone acid (VIII) in ether was treated with diazomethane. Ether was distilled off, and the crystalline reaction product was washed on a filter with ether and crystallized from a benzene-ether mixture. The product (0.85 g) was the syn-cis 4-oxo γ-lactone ester (IX), m.p. 113-115°,

undepressed by admixture of the sample obtained previously (above).

Clemmensen Reduction of the syn-cis 4-Oxo γ-Lactone Acid (VIII) and of its Ester (IX)

a) A mixture of 13.2 g of amalgamated zinc, 33 ml of concentrated hydrochloric acid, 33 ml of methanol, and 6.6 g of the syn-cis 4-oxo γ-lactone acid (VIII) was boiled for one hour, after which a further 30 ml of hydrochloric acid was added and the mixture was boiled for another four hours. On cooling, an oil separated and slowly solidified almost completely. Washing of the product on the filter with 50% aqueous methanol gave 4.8 g of crystals, and recrystallization of these from a large volume of ether gave 3.2 g of pure trans-syn-cis monoester (X), melting constantly at 143-144°.

Found %: C 65.15; 65.02; H 8.49; 8.52 $C_{13}H_{20}O_4$: Calculated %: C 65.01; H 8.33

b) A mixture of 1.5 g of amalgamated zinc, 4 ml of concentrated hydrochloric acid, 4 ml of methanol, and 0.75 g of the syn-cis 4-oxo γ-lactone ester (IX) was boiled for four hours. On cooling, a crystalline product separated and was filtered off and washed with 50% aqueous methanol. The product (0.45 g) was the trans-syn-cis monoester (X). After crystallization from ether it had m.p. 142-143°, undepressed by admixture of the sample obtained previously (above).

trans-syn-cis-Decahydro-1,2-naphthalenedicarboxylic Acid (I), its Anhydride (XI), and its Diester (XII)

a) The trans-syn-cis monoester (X) (2.6 g) was added to a solution of 22 g of potassium hydroxide in 120 ml of water. The mixture was boiled for three hours, filtered, and acidified with hydrochloric acid. Overnight there separated 2.3 g of trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I), m.p. 169-171°, which was crystallized from 30% aqueous acetone and then melted constantly at 175-176° (with decomposition).

Found %: C 63.63; 63.37; H 8.04; 7.99 $C_{12}H_{18}O_4$. Calculated %: C 63.68; H 8.02

Similarly, boiling of 0.4 g of the trans-syn-cis monoester (X) with a solution of 1 g of sodium in methanol for 15 hours, removal of methanol by distillation, boiling of the residue with water, and acidification gave 0.3 g of the trans-syn-cis acid (I). After being crystallized from aqueous acetone it had m.p. 174-175°, undepressed by admixture of the sample described above.

b) In order to obtain the anhydride 2.6 g of the trans-syn-cis acid (I) was boiled with 25 ml of acetyl chloride for one hour, after which volatile substances were distilled off under reduced pressure. The liquid residue solidified when treated with petroleum ether, and it was washed on the filter with a 1 : 1 mixture of diethyl ether and petroleum ether. There remained 1.9 g of the trans-syn-cis anhydride (XI), m.p. 45-46°, unchanged by crystallization from ether.

Found %: C 69.10; 69.13; H 7.75; 7.70 $C_{12}H_{16}O_3$. Calculated %: C 69.21; H 7.74

Hydrolysis of this trans-syn-cis anhydride (XI) with 5% sodium hydroxide solution gave a quantitative yield of the original trans-syn-cis acid (I), and treatment of the anhydride with boiling absolute methanol gave a good yield of the above-described trans-syn-cis monoester (X), m.p. 142-143°.

c) A suspension of 1.7 g of the trans-syn-cis acid (I) in ether was treated with ethereal diazomethane. Solvent was removed, and vacuum distillation of the residue gave 1.6 g of the trans-syn-cis diester (XII), b.p. 149-150° (5 mm); n_D^{20} 1.4823; d_4^{20} 1.1041; found MR 65.67; calculated MR 65.48.

Found %: C 65.95; 66.10; H 8.69; 8.66 $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72

trans-syn-cis Monoester (XIII)

The trans-syn-cis diester (XII) was added to a solution of 0.31 g of potassium hydroxide in 4.5 ml of water and 14.5 ml of methanol, and the mixture was boiled for two hours. Methanol was distilled off under reduced pressure, and the aqueous solution was extracted with ether and acidified with hydrochloric acid. The oil that separated rapidly solidified with formation of 1.1 g of crystals, m.p. 98-103°. Two recrystallizations

from a 1 : 3 mixture of diethyl ether and petroleum ether gave 0.9 g of pure trans-syn-cis monoester (XIII), melting constantly at 106-107°.

Found %: C 64.82; 64.98; H 8.35, 8.28. $C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33

Hydrolysis of the monoester (XIII) with boiling 10% potassium hydroxide solution gave a good yield of the trans-syn-cis acid (I), m.p. 173-174°.

Thermal Isomerization of the trans-syn-cis Anhydride (XI)

The trans-syn-cis anhydride (XI) (0.4 g) was heated for one hour at 250° in a stream of nitrogen and was then distilled at a residual pressure of 20 mm. The liquid product rapidly solidified and was washed on a filter with a 1 : 1 mixture of diethyl ether and petroleum ether. The crystals obtained (0.32 g) melted at 116-120°. Crystallization from a mixture of benzene and petroleum ether gave 0.25 g of pure trans-anti-cis anhydride (XIV), m.p. 127-128°, undepressed by admixture of a sample prepared previously [3].

Isomerization of the trans-syn-cis Monoester (XIII)

The trans-syn-cis monoester (XIII) (0.4 g) was added to a solution of 1 g of sodium in 25 ml of absolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, and the residue was dissolved in 10 ml of water. The solution was filtered and evaporated on a water bath until a thick slurry was obtained. The precipitate of salts was filtered off, washed with absolute methanol, and dissolved in the minimum amount of water. Acidification with hydrochloric acid gave 0.25 g of crystals of m.p. 145-155°, fraction crystallization of which from 30% aqueous acetone gave 0.1 g of trans-anti-trans-decahydro-1,2-naphthalenedicarboxylic acid (XV), which showed no depression of melting point in admixture with a previously prepared sample [1].

SUMMARY

1. Oxidation of the anhydride of 1, 2, 3, 5, 6, 7, 8, 8a-octahydro-1,2-naphthalenedicarboxylic acid (III) with peroxyacetic acid gave the syn-cis 4-hydroxy γ-lactone acid (V), formed by intramolecular lactonization of the epoxide (IV), which is formed intermediately.

2. Chromium trioxide oxidation of the syn-cis 4-hydroxy γ-lactone acid (V) gave the syn-cis 4-oxo γ-lactone acid (VIII), and this product and its ester (IX) were used in the synthesis of trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I). The latter was obtained in good yield by the hydrogenolysis of the 4-oxo γ-lactone acid (VIII), brought about by treatment at the boil with zinc in a mixture of hydrochloric acid and methanol.

3. The trans-syn-cis acid (I) that we have now synthesized is the seventh of the eight possible isomers of decahydro-1,2-naphthalenedicarboxylic acid to be discovered. Its steric transformations were studied with the aid of molecular models. The question of the configuration and stability of the last (eighth) trans-syn-trans isomer (II) was discussed; it is very unlikely to exist under ordinary conditions.

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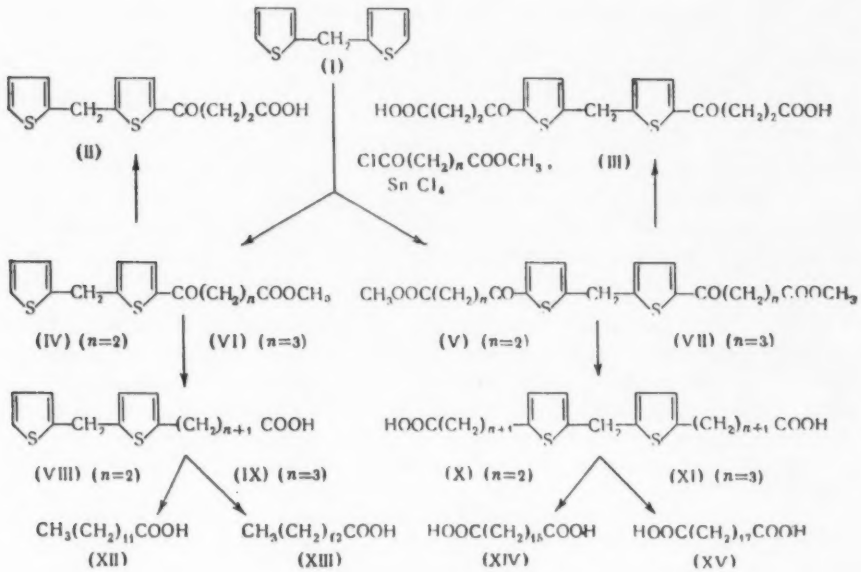
* See C. B. translation.

SYNTHESIS AND REACTIONS OF SOME 2,2'-METHYLENEDITHIOPHENE DERIVATIVES

COMMUNICATION 4. ACIDS OF THE 2,2'-METHYLENEDITHIOPHENE SERIES AND THEIR HYDROGENOLYSIS

Ya. L. Goldfarb and M. L. Kirmalova

In our earlier communications [1, 2] we briefly described a method for the preparation of higher aliphatic mono- and di-carboxylic acids by the reductive desulfurization (hydrogenolysis) of acids of the 2,2'-methylenedithiophene (I) series. We are now in a position to throw more light on this interesting type of reaction of 2,2'-methylenedithiophene:



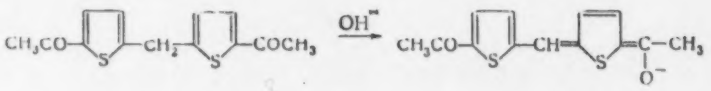
As will be seen, the first stage consists in the synthesis of keto esters. In this respect the method we have selected is similar to that used by several workers for the synthesis of higher fatty acids from thiophene [3].

Almost simultaneously with our results, there appeared a short note by Buu-Hoi and coworkers [4] and a paper by Badger and coworkers [5] which concerned the preparation of undecanedioic and 6,6,-dimethylundecanedioic acids by oxidation of 2,2'-methylenebis- [6] and 2,2'-isopropylidenebis-[5-acetylthiophene], respectively, and hydrogenolysis of the acids formed. The question of the possibility of stopping the reaction at the stage of formation of the monoacetyl compound was not considered by these investigators. It is compounds of the latter type, however, which are essential as a stage in the preparation of monocarboxylic acids from (I).

We acylated 2,2'-methylenedithiophene with methyl 3-(chloroformyl)propionate under conditions close to those described by Papa [7] for thiophene. In this way we obtained a good yield of a mixture of methyl γ-oxo-5-(2-thenyl)-2-thiophenebutyrate (IV) and dimethyl 5,5'-methylenebis[γ-oxo-2-thiophenebutyrate] (V). As our new experiments have shown, decomposition of the complex formed with stannic chloride must be carried out with prolonged stirring with dilute hydrochloric acid in the cold, and not with steam [2], since this induces resinification.

The acid (II) is unstable under the conditions of the hydrolysis of its ester with boiling alcoholic alkali and when subjected to Kizhner reduction; it is obtained in quantitative yield by hydrolysis of the ester at the boil with 10% potassium carbonate solution for one hour. The acid (III) is more stable to the action of alkalis and is reduced without resinification under the conditions proposed by Huang-Minlon [8]. Its dimethyl ester (V) is hydrolyzed considerably more slowly than the ester (IV).

Solutions of the acids (II) and (III) in alcoholic alkali are green, and they turn brown when exposed to the air. A similar phenomenon was observed by Cairns and coworkers for 2,2'-methylenebis[5-acetylthiophene] [6]; these investigators consider that it is to be explained by the formation of a readily oxidized anion in alkaline solution, the structure of this anion being such that it is bound to be colored:



In a similar way, treatment of 2,2'-methylenedithiophene with methyl 4-(chloroformyl)butyrate gave a mixture of methyl δ-oxo-5-(2-thenyl)-2-thiophenevalerate (VI) and dimethyl 5,5'-methylenebis[δ-oxo-2-thiophenevalerate] (VII). When these esters were dissolved in alcoholic alkali, a coloration again occurred.

The monoketo esters (IV) and (VI) were reduced by the Kizhner method as modified by Huang-Minlon for compounds unstable to the action of alkalis [9]. In this way we obtained 5-(2-thenyl)-2-thiophenebutyric and 5-(2-thenyl)-2-thiophenevaleric acids (VIII) and (IX). The diketo diesters (V) and (VII) were reduced by the usual Huang-Minlon method with formation of 5,5'-methylenedi-2-thiophenebutyric and 5,5'-methylenedi-2-thiophenevaleric acids (X) and (XI). Reduction of the esters (IV) and (V) gave poorer yields than that of the esters (VI) and (VII). A similar phenomenon has been observed previously in the Kizhner reduction of γ-keto carboxylic acids [10]. By hydrogenolysis of the acids (VIII) – (XI) with the aid of Raney nickel we obtained tridecanoic, myristic, heptadecanedioic, and nonadecanedioic acids.

At the end of 1955, when our investigation was almost complete, we had the opportunity of acquainting ourselves with the work of Buu-Hoi and coworkers [11], who carried out a six-stage synthesis of hexadecanedioic acid from 2,2'-methylenedithiophene. The first stage consisted in the acylation of (I) with ethyl 5-(chloroformyl) valerate. The resulting monoketo ester was subjected to Kizhner reduction, the product was esterified and then acetylated, and the acetyl group was oxidized to carboxyl. Hence, the method that we proposed [2] for the synthesis of dicarboxylic acids containing an odd number of carbon atoms differs from Buu-Hoi's method in that in the acylation we obtain a diketo dicarboxylic ester directly, so that the synthesis is shorter by three stages.

EXPERIMENTAL

Acylation of 2,2'-Methylenedithiophene with Methyl 3-(Chloroformyl)propionate

a) A solution of 6.0 g (0.04 mole) of methyl 3-(chloroformyl)propionate in 15 ml of dry benzene and a solution of 5.7 g of stannic chloride in 20 ml of dry benzene were added gradually over a period of one hour from two dropping funnels into a stirred solution of 7.2 g (0.04 mole) of (I) in 75 ml of a 2 : 1 mixture of dry benzene and heptane at − 14°. When addition was complete the temperature had risen to − 8°. The mixture was stirred for 15 minutes at this temperature (with longer stirring the complex darkens considerably) and then decomposed with dilute (1 : 9) hydrochloric acid; after 45 minutes the whole of the complex had decomposed. The benzene solution was washed – first with water, then with bicarbonate solution, and again with water – and dried with magnesium sulfate. Solvent was evaporated away, and the residue was vacuum-distilled. Fraction I, b.p. 95-100° (4 mm), 3.6 g, solidified when seeded with a crystal of (I). Fraction II, b.p. 219-220° (4 mm),

4.2 g, solidified when cooled; the crystals were pressed off on a porous plate. After crystallization from alcohol they melted at 34°.

Found %: C 57.55, 57.44; H 4.88, 5.04; S 21.52, 21.69. $C_{14}H_{14}O_3S_2$. Calculated %: C 57.12; H 4.79; S 21.78

The yield of methyl γ-oxo-5-(2-thenyl)-2-thiophenebutyrate (IV) was 72% on the amount of 2,2'-methylenedithiophene that reacted. This ester is soluble in most organic solvents, but is sparingly soluble in petroleum ether and water.

The residue in the flask was washed with dry ether, and 1.35 g (16.8%) of dimethyl 5,5'-methylenebis [γ-oxo-2-thiophenebutyrate] (V), m.p. 84-86°, was obtained. After recrystallization from heptane and then from alcohol (after treatment of the solution with activated charcoal), the melting point was 88-88.5°.

Found %: C 56.24, 56.07; H 5.18, 5.05; S 15.66, 15.58. $C_{19}H_{20}O_6S_2$. Calculated %: C 55.87; H 4.93; S 15.70

The ester is readily soluble in benzene, chloroform, and ethyl acetate, but insoluble in diethyl ether.

b) Acylation of 2,2'-methylenedithiophene (2.7 g, i.e. 0.015 mole) was carried out with two equivalents of the acid chloride, which was added in one portion. The residue obtained after removal of benzene solidifed; it was washed several times with ether and then melted at 84-86°; the yield of the dimethyl ester (V) was 2.7 g. Vacuum fractionation of the ethereal filtrate gave 0.5 g of 2,2'-methylenedithiophene and 1.4 g (39%) of the methyl ester (IV), which came over at 227-230° (4 mm). Both fractions solidified immediately. A further 0.4 g of (V) was isolated from the residue in the flask. The total yield of the dimethyl ester was 62% on the amount of 2,2'-methylenedithiophene that reacted.

Actylation of 2,2'-Methylenedithiophene with Methyl 4-(Chloroformyl)butyrate

a) The acylation of 13.5 g (0.075 mole)of methyl 4-(chloroformyl)butyrate was carried out as described above. After removal of benzene, the residue was fractionated at 4 mm. Fraction I, b.p. 93-99°, 4.7 g, was 2,2'-methylenedithiophene (35% of amount taken). Fraction II, b.p. 220-223°, 10.8 g, was a light-yellow oil which solidified. Fraction III, b.p. 295-305°, 4.3 g, was a thick oil which solidified.

Fraction II was washed with alcohol, and 9.7 g (64.3%) of colorless methyl δ-oxo-5-(2-thenyl)-2-thiophenevalerate (VI), m.p. 48-49,°was obtained. After two recrystallizations from alcohol the melting point was 50-50.5°.

Found %: C 58.51, 58.42; H 5.23, 5.14. $C_{15}H_{16}O_3S_2$. Calculated %: C 58.41; H 5.23

Fraction III was washed with ether, and 2.9 g (13.6%) of colorless crystalline dimethyl 5,5'-methylenebis [δ-oxo-2-thiophenevalerate] (VII), m.p. 72-73°, was obtained. After two recrystallizations from alcohol the melting point was 77-78°.

Found %: C 57.88, 57.89; H 5.57, 5.51. $C_{21}H_{24}O_6S_2$. Calculated %: C 57.77; H 5.54

b) In the acylation of 18g(0.1 mole) of 2,2'-methylenedithiophene with 0.15 mole methyl 4-(chloroformyl) butyrate, the yields of (VI) and (VII) were 8.15 g (32%) and 16.5 g (46%), respectively; 17.8% of the 2,2'-methylenedithiophene was recovered unchanged.

Hydrolysis of the Esters (IV) and (V)

a) A mixture of 3 g of the ester (IV), which was first pressed out on a plate and washed with ethanol,

and 40 ml of 10% potassium carbonate was boiled with stirring for one hour. In the course of this time all the oil went into solution. The solution was cooled and acidified with 1 : 1 hydrochloric acid. The acid (II) was precipitated in almost colorless crystals (2.7 g, i.e. 95%), m.p. 124.5-125°. After recrystallization from 50% alcohol and water it had m.p. 125.5-126.5°. Neutralization equivalent: found 285.9, calculated 280.4.

Found %: C 55.75, 55.73; H 4.33, 4.31; S 22.88, 22.82. $C_{13}H_{12}S_2O_3$. Calculated %: C 55.69; H 4.31; S 22.87

The ester (IV) can be hydrolyzed in good yield also with 2 N alcoholic alkali, and it is then only necessary to warm the mixture gently until the ester is dissolved.

b) The ester (V) was hydrolyzed quantitatively by boiling it with 10% potassium carbonate solution for 4.5 hours. The acid (III) had m.p. 205-207° (from alcohol). Neutralization equivalent: found 191.5, calculated 190.2 [2].

Reduction of Keto Esters

a) A mixture of 4.9 g of the methyl ester (IV), 5 ml of 100% hydrazine hydrate, and 40 ml of diethylene glycol was boiled for 30 minutes. The solution was cooled to 50° and was shaken while a solution of 6.5 g of potassium hydroxide in the minimum amount of water was added slowly through the condenser. The mixture was then boiled for a further 35 minutes, water and excess of hydrazine hydrate were distilled off, and the mixture was boiled at 210° for 90 minutes. The cooled solution was diluted with 50 ml of water, filtered, and acidified with 1 : 1 hydrochloric acid. A thick oil then separated and was quickly extracted with ether. The ether solution was washed twice with water and dried with magnesium sulfate. After evaporation of the ether there remained 2.6 g of a colored solid acid. Recrystallization from heptane gave 2.4 g (54.5%) of 5-(2-thenyl)-2-thiophenebutyric acid (VIII) in the form of snow-white needles, m.p. 48°. Neutralization equivalent: found 267.5, calculated 266.4.

Found %: C 58.76, 58.75; H 5.10, 5.28; S 24.25. $C_{13}H_{14}O_2S_2$. Calculated %: C 58.61; H 5.30; S 24.07

b) Similar treatment of 8.5 g of the methyl ester (VI) gave 7.7 g of crude 5-(2-thenyl)-2-thiophenevaleric acid (IX), m.p. 46-47°. Recrystallization from heptane gave 7.3 g (95%) of the acid in the form of snow-white needles, m.p. 51°. Neutralization equivalent: found 279.4, calculated 280.4.

Found %: C 60.14, 60.09; H 5.55, 5.82; S 22.60, 22.70. $C_{14}H_{16}O_2S_2$. Calculated %: C 59.96; H 5.75; S 22.87

c) A mixture of 8.4 g of the dimethyl ester (VII), 10 ml of 100% hydrazine hydrate, and 50 ml of diethylene glycol was boiled for 30 minutes. The solution was cooled to 40° and 6.5 g of potassium hydroxide was added. The mixture was boiled for 90 minutes, and water and excess of hydrazine hydrate were distilled off. Boiling was then continued for 2.5 hours at 200°. The cooled solution was diluted with 50 ml of water, suspended matter was filtered off, and acidification with concentrated hydrochloric acid then gave a precipitate of 7.1 g of 5,5'-methylenedi-2-thiophenevaleric acid (XI). After recrystallization from 50% alcohol with treatment of the solution with activated charcoal, the melting point was 119-120° and the yield 6.4 g (88%). The melting point was raised to 121.5-122° by recrystallization from 50% acetic acid and a further recrystallization from 50% alcohol.

Neutralization equivalent: found 191.0, calculated 190.25.

Found %: C 60.23, 60.47; H 6.12, 6.33. $C_{15}H_{24}O_4S_2$. Calculated %: C 59.97; H 6.36

d) For the reduction of the acid (III) into 5,5'-methylenedi-2-thiophenebutyric acid (X) see [2].

Hydrogenolysis

a) Myristic acid (XIII). A mixture of 2.5 g of the acid (IX) in 50 ml of 10% sodium carbonate solution, 18 g of Raney nickel [12], and 200 ml of distilled water was heated at 90° for two hours. The precipitate was filtered from the hot solution (no acid could be detected in the filtrate), dissolved in hydrochloric acid, and then extracted with three portions of benzene. The benzene solution was washed with water and dried with magnesium sulfate. After the evaporation of the benzene there remained 1.45 g of myristic acid (XIII). After being recrystallized from 50% alcohol and 80% acetone the acid melted at 53-53.5° (the literature [13] gives m.p. 53.8°). The yield was 72.7%. Neutralization equivalent: found 227.7, calculated 228.4.

Found %: C 73.46, 73.60; H 12.24, 12.30. $C_{14}H_{28}O_2$. Calculated %: C 73.63; H 12.36

b) Tridecanoic acid (XII). The hydrogenolysis of 1.8 g of the acid (VIII) was carried out as described above, and 0.95 g (66%) of tridecanoic acid, m.p. 38°, was isolated. After being crystallized from formic acid with addition of a little acetone and then from 80% acetone, it melted at 40-40.5° (the literature gives m.p. 40.5° [14] and 43° [15]). Neutralization equivalent: found 218.5, calculated 214.3.

Found %: C 72.63, 72.79; H 12.15, 12.22. $C_{13}H_{26}O_2$. Calculated %: C 72.37; H 12.23

c) Nonadecanedioic acid (XV). The acid (XI) (2.5 g, m.p. 119-120°) was subjected to hydrogenolysis under the above-described conditions. From the hot alkaline filtrate, 0.9 g of the acid (XV), m.p. 119°, was isolated. The precipitate was washed with hot sodium carbonate solution (no acid could be detected in the filtrate) and treated with hydrochloric acid. The insoluble part was filtered off and washed with water and three portions of hot methanol. From the methanol solution 0.6 g of the acid was isolated. The total yield of the acid (XV) was 69.4%. After being crystallized from benzene and acetone the acid melted at 121° (the literature gives m.p. 119° [16] and 121-121.6° [17]). Neutralization equivalent: found 162.8, calculated 164.24.

Found %: C 69.16, 69.31; H 11.16, 11.16. $C_{19}H_{36}O_4$. Calculated %: C 69.47; H 11.05

d) Heptadecanedioic acid (XIV). For the preparation of this acid see [2].

SUMMARY

1. A study was made of the conditions required for the acylation of 2,2'-methylenedithiophene with acid chlorides of monoesters of dicarboxylic acids (ω-(chloroformyl)alkanoic esters), the hydrolysis of the resulting keto esters, and their Kizhner reduction.

2. By hydrogenolysis with the aid of Raney nickel, tridecanoic, myristic, heptadecanedioic, and nonadecanedioic acids were prepared.

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TRANSFORMATIONS OF BUTYLBENZENE IN PRESENCE OF A NICKEL – ALUMINA CATALYST AT HIGH TEMPERATURES UNDER HIGH PRESSURES OF HYDROGEN

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Several investigations have been devoted to the transformations of butylbenzene in presence of various oxide catalysts at elevated temperatures [1-5]. Moldavsky and Kamusher [3] described the transformations of butylbenzene in presence of a chromium oxide catalyst at 472°: the catalyzate contained 12% of alkenes and 12% of naphthalene. Grosse [4] investigated the behavior of butylbenzene in presence of a chromia-alumina catalyst at 500° and observed the formation of up to 55% of naphthalene. The transformations of butylbenzene were studied in greatest detail by Nametkin, Khotimskaya, and Rozenberg [5] in presence of a chromia-alumina catalyst. At 520° at a space velocity of 0.25 hour^{-1}, butylbenzene gave about 75% of catalyzate containing about 43% of naphthalene in admixture with lower benzene homologs, probably formed by partial elimination of the butylbenzene side chain.

Moldavsky and Bezdel [6] found that the readiness with which the alkyl group is eliminated in the form of the corresponding alkene depends on the degree of polarization of the bond between the radical and the nucleus. It was found that the strength of the bond between the aromatic nucleus and the radical falls along the series:

$$— CH_3 > — C_2H_5 — CH(CH_3)_2 > — C(CH_3)_3.$$

In the study of the transformations of some aromatic hydrocarbons in presence of some oxide-metal catalysts [7, 8] we showed that at 460° under high pressures these hydrocarbons undergo various profound transformations. We found that in these cases high pressure of hydrogen favors hydrogenolysis, both of the bond between the aliphatic radical and the nucleus and of C—C bonds in the side chain.

In continuation of our earlier investigations, we considered it to be of interest to study the behavior of butylbenzene over a nickel-alumina catalyst at high temperatures under high pressures of hydrogen. It was found that the main type of transformation of butylbenzene at 350-465° in presence of hydrogen at 25 or 50 atm is partial and complete hydrogenolysis of the side chain with formation of propylbenzene, ethylbenzene, toluene, and benzene. Under these conditions dehydrocyclization of butylbenzene to naphthalene did not proceed to a great extent.

EXPERIMENTAL

The butylbenzene was synthesized by the Wurtz reaction: by the action of sodium on a mixture of bromobenzene and butyl bromide [9]. In the fractionation of the resulting mixture of hydrocarbons through a 42-plate column a fraction was collected having b.p. 182.5-183.1° (757 mm), n_D^{20} 1.4830 and d_4^{20} 0.8613; found MR 48.57; calculated $C_{10}H_{14}$ MR 48.40.

The nickel-alumina catalyst used in the investigation was prepared as described previously [10]. The content of reduced nickel in the catalyst was 30%. Its hydrogenating and dehydrogenating properties were determined from the extent of conversion of benzene at 180° and of cyclohexane at 300°.

Experiments on the catalytic transformations of butylbenzene were carried out at various temperatures and pressures of hydrogen at a space velocity of 0.8 hour^{-1} and a molar ratio of hydrogen : hydrocarbon equal

to 5 : 1 in a flow apparatus which, together with the experimental and analytical procedure, has been described previously [7, 11]. For each experiment we took 250 g of butylbenzene. In order that the investigation might be as complete and reliable as possible, after the experiments at various temperatures and pressures we carried out a second series of experiments under the same conditions, and it was found that the transformations of butylbenzene in the first and second series were almost identical. Table 1 gives results on the catalysis of butylbenzene in presence of 30% Ni – Al_2O_3.

TABLE 1

Properties of Butylbenzene Catalyzates

Experiment	Experimental conditions		Properties of catalyzate		Yield of catalyzate (%)	Conversion (%)
	Pressure (atm)	Temperature (°C)	n_D^{20}	d_4^{20}		
1	25	350	1.4890	0.8535	82.0	21.8
2	25	400	1.4905	0.8569	79.8	43.0
3	25	465	1.4980	0.8627	67.7	92.0
4	50	400	1.4915	0.8561	81.5	41.7
5	50	450	1.4975	0.8621	68.8	96.2
6	50	465	1.4985	0.8657	64.5	95.6

The results in Table 1 on reaction in presence of 30% nickel-alumina catalyst show that with rise in temperature from 350° to 465° (Experiments 1-3) there is a sharp increase in the percent conversion of butylbenzene from 21.8 to 92.0. Change in pressure from 25 to 50 atm has no substantial effect on the degree of conversion and kind of transformation of butylbenzene.

The catalyzates were fractionated through a 42-plate column. The results of analytical fractionation of butylbenzene catalyzates are given in Table 2. In all cases a 100-ml portion of catalyzate was taken for fractionation.

TABLE 2

Hydrocarbon Contents (% by weight) in Butylbenzene Catalyzates.

Expt.	Fraction boiling up to 78.5°	Benzene	Toluene	Ethylbenzene	Xylene Fraction (137-145°)	Propylbenzene fraction (157-161°)	Fraction of b.p. 163-182.6°	Butylbenzene	Naphthalene
1	2.0	8.6	4.8	3.4	0.4	0.5	1.5	78.3	0.3
2	1.8	13.5	9.3	8.5	1.8	1.0	5.6	57.0	0.5
3	1.3	25.4	20.2	14.0	2.8	1.0	16.0	8.1	6.3
4	1.7	13.6	9.2	8.6	1.6	0.8	5.6	58.0	0.6
5	2.0	29.1	21.1	25.4	2.1	1.2	10.8	4.3	4.7
6	1.9	27.3	19.3	26.2	2.3	0.9	10.5	3.2	5.1

The individual hydrocarbons isolated from the catalyzates had properties close to those described in the literature, and their values are therefore not given in Table 2.

The combined 71-78.5° fractions of catalyzates from Experiments 1-6 (10.3 ml; n_D^{20} 1.4720 and d_4^{20} 0.8215) were subjected to chromatographic separation on silica gel. The dearomatized part of this combined fraction (5.1 ml) boiled over the range 70-79.2° (751 mm) and had n_D^{20} 1.4120 and d_4^{20} 0.7492; it was investigated by the optical (Raman spectrum) method.* It was shown (on the basis of a set of analytically important lines) that the fraction contained methylcyclopentane (about 60%), cyclohexane (about 15%), and hexane isomers (about 10%).

* The optical analysis was carried out by Yu. P. Egorov, to whom the authors express their thanks.

The xylene fractions from the catalyzates of Experiments 3-6 were united and oxidized by Ullmann's method (with alkaline permanganate) [12]. Separation of the resulting acids was carried out by the method described by Moldavsky and coworkers [13]. From the oxidation products of these fractions we isolated benzoic, phthalic, isophthalic, and terephthalic acids; the last two acids were converted into their methyl esters, which melted at 65.6° and 139°, respectively. The oxidation results are given in Table 3.

TABLE 3

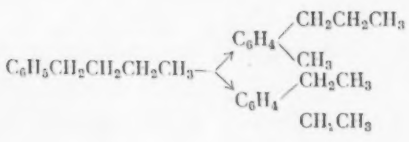
Composition of Combined Xylene Fraction (b.p. 137-145°)

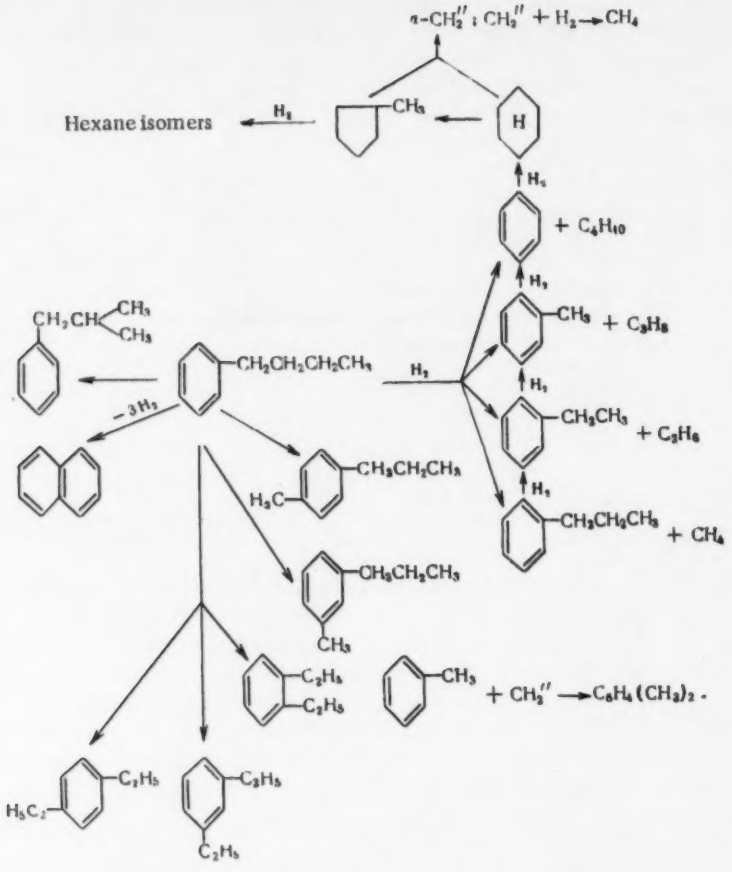
Experiment	Amount taken for oxidation (g)	Amount of mixture of acids (g)	Content (%) of			
			of m-xylene	p-xylene	o-xylene	alkyl-benzene
3	4.5	3.96	49.0	36.0	10.0	5.0
4	3.1	2.87	53.5	35.5	8.0	3.0
5	4.2	4.12	57.3	31.7	5.9	5.1
6	4.3	3.91	56.5	34.5	6.0	3.0

The combined fractions of catalysts from Experiments 3, 5, and 6 having b.p. 163-182.6°, d_4^{20} 0.8630 and n_D^{20} 1.4979 were separated into two parts by fractionation through a 42-plate column: one part (16.4 g; b.p. 160-173.5°, n_D^{20} 1.4875 and d_4^{20} 0.8541) was subjected to Ullmann oxidation [12]. Benzoic acid, m.p. 121°, was isolated. Comparison of the properties of this fraction with those reported [14] for isobutylbenzene (b.p. 172.8°, n_D^{20} 1.4865, d_4^{20} 0.8535) enables us to conclude that it consisted essentially of isobutylbenzene. The second part of the fraction (18.2 g), b.p. 173.5-182.6°, n_D^{20} 1.4949 and d_4^{20} 0.8627, was also oxidized with permanganate. Separation of the crystalline acids obtained by the method of Moldavsky and coworkers [13] showed that the acid mixture contained 9.3% of phthalic, 54.3% of isophthalic, and 35% of terephthalic acid.

The formation of benzenedicarboxylic acids must be attributed to the oxidation of o-, m-, and p-propyltoluenes and of diethylbenzenes. In the Raman-spectrum analysis of this fraction, frequencies associated with m- and p-propyltoluenes and the three isomeric diethylbenzenes were found. From the dark-yellow residues obtained in the fractionation of butylbenzene catalyzates we isolated 17.6 g of naphthalene, which, after being sublimed, melted at 79.5°; m.p. of picrate 149°.

It follows from the results of the analysis of the catalyzates that, under the given conditions, butylbenzene undergoes complex transformations with formation of products of its complete and partial dealkylation: benzene, toluene, ethylbenzene, and propylbenzene. Benzene, toluene, and ethylbenzene were obtained in the highest yields; the yield of the propylbenzene fraction (b.p. 157-161°) was considerably less. The results indicate that a high pressure of hydrogen favors the hydrogenolysis of a C – C bond in the side chain. In addition to this main reaction there are other reactions that proceed to a quite appreciable extent, namely, hydrogenation of the benzene ring, contraction of the cyclohexane ring to a five-membered ring, hydrogenolysis of the cyclopentane compounds, and cyclization of aliphatic side chain of butylbenzene with formation of naphthalene. Also, under the catalysis conditions dialkylbenzenes are also formed, namely, xylenes, propyltoluenes, and diethylbenzenes. The mechanism by which these hydrocarbons are formed is at present obscure. It may only be supposed that C_{10} hydrocarbons (propyltoluenes and diethylbenzenes) are formed by a peculiar isomerization of butylbenzene.





As regards the formation of xylenes, the possibility cannot be excluded of their formation in the methylation of toluene by methylene radicals arising at the catalyst surface by partial decomposition of cycloalkanes:

$$C_6H_5CH_3 + CH_2'' \rightarrow C_6H_4(CH_3)_2.$$

On the basis of the results of the investigation of the catalyzates the reactions occurring in the catalysis of butylbenzene over a nickel-alumina catalyst can be presented in the accompanying scheme.

SUMMARY

1. An investigation was made of the transformations of butylbenzene in presence of a 30% nickel-alumina catalyst and hydrogen under pressure (25 and 50 atm) at various temperatures (350, 400, 450, and 465°) in a flow system.

2. It was shown that rise in temperature from 350° to 465° is accompanied by increase in the percent conversion of butylbenzene from 21.8 to 92.

3. In the catalysis of butylbenzene hydrogenolysis of the side chain occurs with formation of benzene, toluene, ethylbenzene, and propylbenzene.

4. It was shown that increase in pressure of hydrogen favors rupture of C – C bonds in the side chain of butylbenzene.

5. Hydrogenolysis of the side chain of butylbenzene is accompanied by hydrogenation of the benzene

nucleus, contraction of a six-membered ring to a five-membered ring, hydrogenolysis of the latter, formation of xylenes, propyltoluenes, and diethylbenzenes, and dehydrocyclization of the side chain of butylbenzene with formation of naphthalene.

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* [See C. B. translation].

COPOLYMERIZATION OF DIENIC HYDROCARBONS WITH ALKYL VINYL ETHERS

COMMUNICATION 2. LOW-TEMPERATURE EMULSION COPOLYMERIZATION OF BUTADIENE WITH ALKYL VINYL ETHERS

S. N. Ushakov, S. P. Mitsengendler, and V. N. Krasulina

The copolymerization of unsaturated monomers provides one of the most effective methods of modifying the properties of a polymer. In its application to dienes this method has received extensive use in the manufacture of synthetic rubber (copolymerization of dienes with vinyl compounds).

Alkyl vinyl ethers are among the few vinyl monomers which have not yet been investigated for use in combination with dienic hydrocarbons, in particular butadiene (the literature consists only in a few patents [1-3]). The effect of the presence of ether units on the properties of polybutadiene rubber has not been determined. This is to be explained mainly by the difficulty of introducing ether units into the polybutadiene chain. The method that we have described for the preparation of such copolymers in presence of carbon tetrachloride [4] makes it possible to obtain copolymers having a preponderance of ether units, but their molecular weights are low (3000-4000).

The present work had the object of preparing copolymers of butadiene and alkyl vinyl ethers of high molecular weight and of determining the effect of the presence of ether units on the properties of polybutadiene. For this purpose we made use of the method of low-temperature emulsion polymerization.

EXPERIMENTAL

The experiments were carried out in sealed tubes, 20-25 mm in diameter. The tubes were fixed to a rotating disk in a water thermostat at 65°. In the case of low-temperature copolymerization, agitation was effected by means of a shaker situated in a cold, constant-temperature box. Isolation of the copolymer was carried out either by freezing the latex in solid carbon dioxide or by precipitation with acetone. The copolymer was purified by precipitation with methanol from benzene solution in presence of 0.2% of stabilizer (N-phenyl-2-naphthylamine). Unlike polybutadiene, the copolymers were readily soluble in benzene, even in absence of "regulator". The copolymers, dried to constant weight at room temperature, were analyzed by Liebig's method for carbon content. In certain cases chlorine content and unsaturation were determined. Molecular weights were determined osmometrically.

Low-temperature polymerization was carried out in presence of an oxidation-reduction system of iron sulfate, sodium pyrophosphate, and glucose [5]. The initiators used were benzoyl peroxide (BP) and cumene hydroperoxide (CHP) [α,α-dimethylbenzyl hydroperoxide].

Low-temperature Emulsion Copolymerization of Butadiene with Alkyl Vinyl Ethers

The operation of copolymerizing these systems in emulsions is complicated by the instability of alkyl vinyl ethers in acid, and even in alkaline, aqueous media. It is known that copolymerization in a neutral medium is extremely slow. Experiments on emulsion copolymerization at 50-60° gave no positive results: the ether partially or completely decomposed with formation of acetaldehyde and an alcohol. The formation of these could be the reason for the stopping of the process. Only when we went over to low temperatures (4-5°) and used an oxidation-reduction system would the reaction proceed in an alkaline medium. Even under

low-temperature conditions the pH of the medium was of great importance (Table 1). In an acid medium polymerization did not occur.

TABLE 1

Effect of the pH of the Aqueous Phase on the Yield of Copolymer for Equimolecular Proportions of Butadiene and Isopropyl Vinyl Ether at 4-10°

pH	Duration of polymerization (hours)	Yield of copolymer (% by weight)	Notes
12.5	69	12	Initiator:
10.0	69	10	2% of benzoyl
8.5	69	8.5	peroxide + 20%
7.0	69	7	of CCl_4
5.5	69	Traces	

The simultaneous operation of two mechanisms on account of the specific action of carbon tetrachloride, such as we observed in mass polymerization [4], is not found to any appreciable extent in emulsion copolymerization.

The compositions of emulsion copolymers obtained in presence of carbon tetrachloride are almost the same as those of copolymers obtained in absence of carbon tetrachloride (Table 2, Experiments 4 and 5, 16 and 17).

TABLE 2

Effect of Carbon Tetrachloride on the Emulsion Copolymerization of Butadiene (4% of potassium stearate as emulsifier) with Isopropyl and Butyl Vinyl Ethers.

Expt.	Ether	Content of		Content of initiator (%)		pH	Temperature (°C)	Duration of polymerization (hours)	Yield (% by weight)	Ether content of copolymer (mole %)	Notes
		Ether in original mixture (mole %)	CCl_4 (%)	CHP	BP						
11	Isopropyl	50	20	–	2	–	65	56	63.6	71	Mass polym.
54	vinyl ether	50	20	–	1	10	65	69	15.0	17	Liquid polymer
56		50	20	0.15	–	8.5	4	94	14.5	18	
4		50	20	0.30	–	12.0	4	84	22.8	4.9	
5	Butyl	50	0.0	0.30	–	12.0	4	96	40.0	3.0	
16	vinyl	50	20	0.30	–	12.0	20	104	28.0	5.9	
17	ether	50	0.0	0.30	–	12.0	20	96	40.0	3.0	

When the pH of the aqueous medium is lower, e.g. 8.5-10, the ether content of the copolymer can be increased at the expense of reduction in yield (Experiments 54 and 56). With addition of 20% of carbon tetrachloride, in all cases only copolymers with a predominance of butadiene are obtained, in accord with its activity in free-radical copolymerization. Replacement of benzoyl peroxide by cumene hydroperoxide has no essential effect on the process. By increase in the ether content of the original mixture its content in the

copolymer can be increased up to 19%. However, the yield and molecular weight of the copolymer are then correspondingly reduced (Tables 3 and 4).

TABLE 3

Effect of Ether Concentration on the Yield and Composition of the Copolymer.

Experiment	Content of: Ether in original mixture (mole %)	CHP (%)	CCl_4 (%)	Duration of polymerization (hours)	Yield (% by weight)	Ether content of copolymer (mole %)	Notes
5	50	0.5	0.0	84	35.0	3.0	
4	50	0.5	20.0	84	22.8	5.0	
8	66	0.5	20.0	140	13.0	9.3	Butyl vinyl ether
12	66	0.5	20.0	140	17.5	9.2	
10	80	0.5	20.0	140	6.0	—	
43	80	0.15	—	42	5.0	19.2	Isopropyl vinyl ether

TABLE 4

Effect of Initial Concentration of Butyl Vinyl Ether on the Molecular Weight of the Copolymer.

Name	Ether content (mole %)	Molecular weight	Notes
Copolymer	0.0	108 000	
"	5.9	53 000	Emulsion polymerization
"	18.0	26 500	
"	25.0	3 000	Mass copolymer

TABLE 5

Effect of Presence of Ether Units in Copolymer of Vitrification Temperature and Chemical Stability.

Isopropyl vinyl ether				
Ether content of copolymer (moles %)	Vitrification temperature (°C)	Swelling in 24 hours (%) in: Benzene	Gasoline	3 : 1 gasoline + benzene
6.2	—83	111.5	53	72.2
10.7	—81	97.7	50	66.2
16.3	—84	97.0	50.7	68.4
18.2	—83	69.7	30.3	43.5
70.0	—31	56.0	—	—

The emulsion copolymers contained only 0.1-0.2% of halogen, instead of the 1-2% present in mass polymers; this is associated with their higher molecular weight. The reduction in yield and molecular weight of copolymers with increase in ether content illustrates the inhibiting action of alkyl vinyl ethers (Table 4).

Determination of the physicomechanical properties of copolymers differing in ether content showed that the presence of a small proportion (up to 18%) of ether units in polybutadiene has little effect on the vitrification temperature (− 84°), which is close to that of polybutadiene. When ether units predominate in the copolymer (mass copolymer), the vitrification temperature rises and is close to that of the polyether (− 31°). In this case the solubility in hydrocarbons is much reduced (Table 5).

SUMMARY

1. In the emulsion copolymerization of butadiene with alkyl vinyl ethers in an alkaline medium the specific action of carbon tetrachloride is suppressed and the process proceeds almost entirely by the free-radical mechanism.

2. Introduction of ether units greatly reduces the molecular weight of polybutadiene (from 108,000 to 3,000).

3. The introduction of up to 20% of ether units in the polybutadiene chain has little effect on its stability to frost ($T_v = -84°$). When there is a predominance of ether units (70%), the stability to frost is greatly reduced ($T_v = -31°$), though the chemical stability is increased.

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REACTIONS OF FREE RADICALS IN SOLUTIONS

COMMUNICATION 8. REACTIONS OF FREE 1-CYANO-1-METHYLETHYL AND METHYL RADICALS WITH 1-HEPTENE, α-METHYLSTYRENE, AND ISOBUTENE

E. B. Milovskaya, B. A. Dolgoplosk, and B. L. Erusalimsky

The study of the reactions of free radicals with unsaturated compounds is of considerable interest in connection with the investigation of the main and side reactions proceeding with participation of free radicals in the polymerization process. Quantitative data on the direction of attack of free radicals in the primary acts and on the character of the further changes can be obtained only by the use of suitable model systems. Also, the reactions of free radicals with unsaturated compounds of the olefin series comprise a comparatively little studied field.

The most systematic investigations, carried out by Haszeldine [1, 2] and others, are concerned with a very specific group of compounds – haloolefins and halogen-containing free radicals – and therefore have an interest of a special character. In the investigations of Kharash [3] and Kooyman [4] attention is directed mainly on the CCl_3 free radical. Cramer [5] and Szwarc [6], who studied the reactions of free ethyl and methyl radicals with compounds of various classes, estimated the extent of reaction only indirectly; they did not study the products formed by the addition of free radicals at unsaturated bonds. The way in which free methyl and ethyl radicals react with olefins, in particular with propene and the butenes, was investigated more fully by Rust and others [7].

The present paper is concerned mainly with the study of the composition of products formed by reaction between free radicals and compounds containing an ethylenic bond, namely, 1-heptene, α-methylstyrene, and isobutene, with the object of estimating the relative contributions of the competing reactions of addition to unsaturated bonds, removal of an H atom, recombination, and disproportionation. The investigation of the products of the reaction of free radicals with α-methylstyrene is particularly interesting because this compound, which does not polymerize in presence of free radicals, nevertheless readily copolymerizes with other monomers. Much of the work was carried out with 1-cyano-1-methylethyl radicals formed by the thermal decomposition of 2,2'-azobis[2-methylpropionitrile] in accordance with the equation:

$$(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2 \rightarrow 2(CH_3)_2C(CN)\cdot + N_2 \qquad (1)$$

The paper also gives data characterizing the extent to which H atoms may be removed from certain hydrocarbons by a free methyl radical. The choice of the 1-cyano-1-methylethyl radical was determined by the fact that it is of comparatively low activity in the reaction of removal of an H atom, so that the effects of side reactions associated with this act are almost excluded. It follows from data given in a previous communication [8] that the reaction

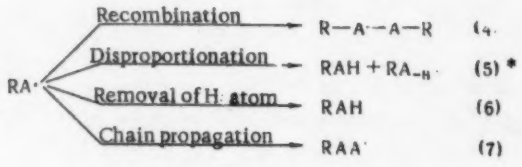
$$(CH_3)_2C(CN)\cdot + LH \rightarrow (CH_3)_2CH(CN) + L\cdot \qquad (2)$$

proceeds to an appreciable extent in sufficiently dilute solutions (1.2-1.3 mole %). At higher concentrations of the azo dinitrile (5 mole % and higher) the formation of isobutyronitrile appears to result from the disproportionation of free radicals:

$$2\,(CH_3)_2\dot{C}(CN) \rightarrow (CH_3)_2CH(CN) + CH_3-C(CN)=CH_2, \qquad (3)$$

a conclusion derived not only from the results of the present investigation, but also from the results of others [9, 10].

As will be shown below, the primary reaction of free radicals R· with molecules of the unsaturated compound A with formation of a new free radical RA· can result, according to the nature of the component A, in the formation of the following compounds:



It follows from our results that the last of these reactions is terminated mainly on account of acts of recombination. In addition to these reactions (3-7), formation of tetramethylsuccinonitrile (R—R) occurs to a considerable extent in all cases:

$$2\,(CH_3)_2\dot{C}(CN) \rightarrow (CH_3)_2C(CN)-C(CN)(CH_3)_2. \qquad (8)$$

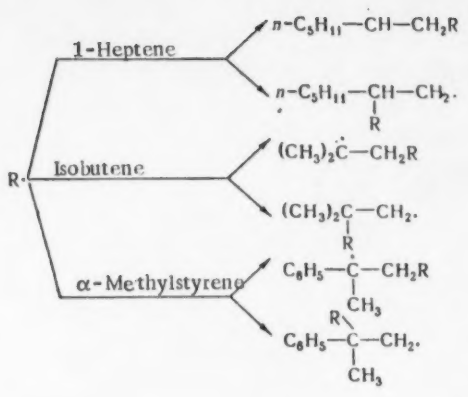
We must take account of the possibility that a substantial proportion of the product R — R is formed as a result of primary recombination, i.e. the so-called "cage effect". According to Bevington [11], in the thermal decomposition of 2,2'-azobis[2-methylpropionitrile] in solution the extent to which the primary recombination reaction occurs attains 30%.

The principal results of our experiments are summarized in Table 1.

The relations between the yields of the products of reaction of free radicals with the hydrocarbons studied are clearer when we exclude compounds formed without the participation of these hydrocarbons, i.e. the products RR and RH, from the general material balance. Values calculated in this way are given in Table 2.

The main reaction products are very similar in character for 1-heptene and isobutene. In both cases the principal reaction product is R — A — A —R, the formation of which corresponds to Equation (4). For α-methylstyrene Reaction (5) is predominant, the products of the disproportionation of RA· free radicals being formed. It must be pointed out that, in principle, the primary reaction between the free radical and the unsaturated compound may take one of two directions:

* Here and in the sequel, RA_{-H} is the conventional denotation of the unsaturated component formed in the disproportionation of RA· free radicals.



(9a)

(9b)

(10a)

(10b)

(11a)

(11b)

TABLE 1

Compositions of Products Formed in the Decomposition of 2,2'-Azobis [2-methylpropionitrile] in Various Media (at 80°).

Unsaturated component	Concentration of 2,2'-azobis[2-methylpropionitrile], mole %	Yields of products (%)								Content of R in products not characterized in the form of individual compounds (% calculated from %N)	Total R in reaction products (% of theoretical amount)
		R—R	R—H	RAH	RA_{-H}	RAAR	R_2A_2	R_3A_2	R_3A_3		
1-Heptene	20	55.5	2.7	5.5	—	22.0	8.4	—	—	—	94.1
α-Methylstyrene	5	34.7	3.9	26.5	26.5	—	—	—	—	12	103.6
Isobutene	5	27.0	3.7	—	—	23.0	—	15.5	6.6	6	81.8

On the basis of the usual view of reactions proceeding predominantly in the direction of the formation of the most stable products, Reactions (9a), (10a), and (11a) must be regarded as the most probable since they lead to relatively more stable free radicals. This inference finds direct confirmation in our results for α-methylstyrene. The fact that in this case disproportionation products are formed in high yield indicates that the addition of 1-cyano-1-methylethyl radicals is effected in a manner associated with the formation of tertiary free radicals. The disproportionation of the radicals which would be formed by Equation (11b) does not appear to be possible. For α-methylstyrene the disproportionation of RA· free radicals may give unsaturated compounds of various structures:

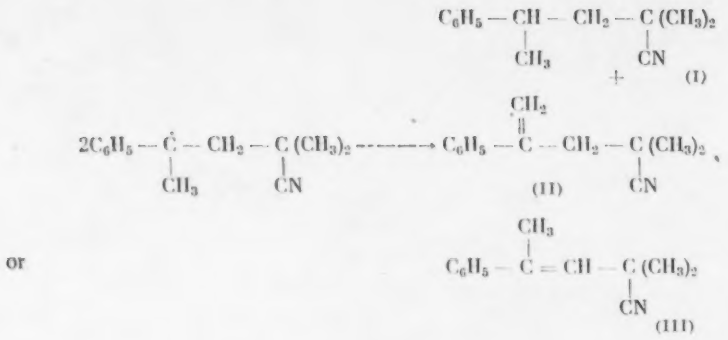


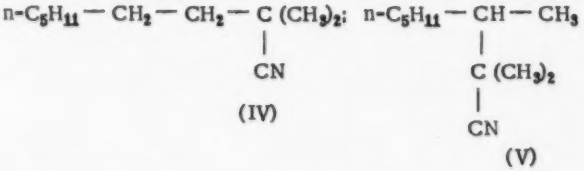
TABLE 2

Yields of Products of Reaction of $(CH_3)_2\dot{C}CN$ Radicals • with Hydrocarbons.

Hydrocarbon	Yield (%)					
	RAH	RA_{-H}	RAAR	R_2A_2	R_2A_2	R_2A_2
1-Heptene	13.2	—	52.5	20.1	—	—
α-Methylstyrene	43.2	43.2	—	—	—	—
Isobutene	—	—	33.0	—	22.4	9.5

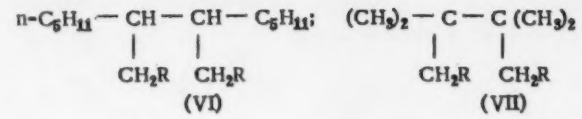
• As 100% is taken the total amount of radicals taking part in the reaction less the amount associated with the formation of the products R — R and RH.

Ozonization results showed that the unsaturated compound formed had a structure corresponding to Formula (II). Among the ozonolysis products we detected formaldehyde (13.5%), formic acid (48%), and the ketone $C_6H_5 - CO - CH_2C(CN)(CH_3)_2$, which was characterized by its semicarbazone. Acetophenone, which would have been formed in the ozonolysis of the compound (III), was not found among the ozonolysis products. As will be seen from Table 1, when the decomposition of 2,2'-azobis[2-methylpropionitrile] is carried out in a 1-heptene medium, an appreciable amount of the product RAH is formed. We showed that, in this case, after distillation of unchanged hydrocarbon from the reaction mixture, no unsaturated compounds were present. This fact enables us to conclude that for heptene the product RAH is formed not by the disproportionation reaction, but by Reaction (6), i.e. by removal of an H atom from a solvent molecule or other components of the system. In accordance with Reactions (9a) and (9b), this compound must be assigned one of two structures:



The above considerations suggest that Structure (IV) is the most probable. On the same basis the products R— A — A — R, formed by reaction of free radicals with 1-heptene and with isobutene, must be assigned

the following structures •:



(VI) (VII)

in which R is the 1-cyano-1-methylethyl radical.

In the case of isobutene some more complex compounds were isolated; in analysis they corresponded to $C_{20}H_{34}N_3$ and $C_{24}H_{42}N_3$, i.e. to R_3A_2 and R_3A_3, respectively. The formation of such compounds is most probably associated with the appearance of new unsaturated products in the course of reaction as a result of acts of disproportionation and the further interaction of these with free radicals. The fact that acts of disproportionation occur in this case is confirmed by the presence of an appreciable amount of unsaturated compounds in one of the fractions (see Experimental). The higher yield of products of the recombination of free 1-cyano-1-methylethyl radicals (R — R) in reaction in 1-heptene is probably associated with the fact that in this case we are dealing with a considerably higher concentration of the azo dinitrile than in the cases of isobutene and α-methylstyrene.

Comparison of yields of isobutyronitrile (RH) leads to the conclusion that the nature of the unsaturated component has no substantial effect on the yield of this compound, which varies from 3 to 4% for all the hydrocarbons studied. On the other hand, as the results given in Table 2 show, even such a highly active free radical as methyl cannot remove an H atom from an α-methylstyrene molecule. It follows that isobutyronitrile is formed not by Reaction (2), but as the result of the disproportionation of free 1-cyano-1-methylethyl radicals (Reaction (3)).

A clear idea of the difference in relative activity between 1-heptene and α-methylstyrene was obtained from a study of the reactions of these hydrocarbons with free methyl radicals. As a source of $CH_3\cdot$ radicals we used 1-methyl-3-phenyltriazene, which decomposes as follows when heated in solution:

$$C_6H_5 — NH — N = N — CH_3 \rightarrow C_6H_5NH\cdot + N_2 + CH_3\cdot \qquad (12)$$

The yield of methane obtained when the decomposition reaction is carried out in a given medium characterizes the extent of reaction between $CH_3\cdot$ radicals and the given medium:

$$CH_3\cdot + LH \rightarrow CH_4 + L\cdot \qquad (13)$$

As indicated in a previous communication [8], for compounds having particularly mobile H atoms the yield of methane in the decomposition of methylphenyltriazene exceeds 60%. In the present investigation we obtained data on the yields of methane in heptane, 1-heptene, and α-methylstyrene media (Table 3).

The results show that the presence of ethylenic double bonds in a hydrocarbon greatly reduces the contribution of Reaction (13). Already in the case of 1-heptene we may consider that, of the two competing reactions (removal of H atoms by free radicals and addition of free radicals at double bonds), the principal part is played by the second. In the case of α-methylstyrene, Reaction (13) is completely suppressed: the free radicals are taken up quantitatively by the double bonds.

The sharp distinction between external (vinyl) and internal double bonds in their reactivities toward free radicals will be clear from comparison of the results given in Table 3 with results published by us previously [8]. In the investigation cited it was shown that reaction of free radicals with cyclohexene gives a somewhat higher yield of methane (61%) than that found for cumene (56%). It follows that the presence of internal double bonds, which results in higher mobility of hydrogen atoms, favors removal of H atoms by free radicals.

• Compounds (IV), (VI), and (VII) were characterized by elementary composition. Their structures were not studied.

TABLE 3

Yields of Methane in the Decomposition of 1- Methyl-3-phenyltriazene in Various Hydrocarbons.

Hydrocarbon	Triazene concentration (mole %)	Temperature (°C)	Yield of methane (%)
Heptane	10	100	55
1-Heptene	10	100	16
α-Methylstyrene	10	100	0

EXPERIMENTAL

The procedure used in the decomposition of the initiators and in the investigation of the decomposition products was essentially as described previously [8]. Experiments with isobutene were carried out in an autoclave. Most of the tetramethylsuccinonitrile crystallized out after removal of unchanged solvent by distillation. Some of this dinitrile was distilled off in the course of the fractionation of residue. Isobutyronitrile, the yield of which varied from 0.4 to 0.6 g, was not isolated as an individual compound, but was determined by hydrolysis of the corresponding fractions (b.p. of nitrile 107-108°) by the procedure* described by Kooyman and others [12].

Products of the decomposition of 2,2'-azobis[2-methylpropionitrile] in 1-heptene. A mixture of 18.1 g of 2,2'-azobis[2-methylpropionitrile] and 54.1 g of 1-heptene was heated at 80° until nitrogen ceased to be liberated (six hours). The following products were isolated from the reaction mixture:

a) $C_{11}H_{21}N$ (RA_H); b.p. 78-79° (3 mm); d_4^{20} 0.8189; n_D^{20} 1.4311; found MR 52.8; calculated for $C_{11}H_{21}N$, MR 52.8; found M 163; calculated M 167; yield 2 g (5.5%).

Found %: C 78.98, 79.26; H 12.12, 12.33; N 8.38, 8.68. $C_{11}H_{21}N$. Calculated %: C 79.04; H 12.57; N 8.39

b) $C_{22}H_{40}N_2$ (RAAR); b.p. 191-192° (1 mm); d_4^{20} 0.8814; n_D^{20} 1.4620; found MR 103.5; calculated for $C_{22}H_{40}N_2$ MR 103.4; found M 282; 276; calculated M 332; yield 8 g (22%).

Found %: C 79.45, 78.83; H 12.14, 12.42; N 8.51, 8.90. $C_{22}H_{40}N_2$. Calculated %: C 79.5; H 12.04; N 8.4

c) $C_{29}H_{54}N_2$ (R_2A_3); did not distill when heated to 200° (1-2 mm); yield 4 g (8.4%); found M 422; 445; calculated M 430.

Found %: N 7.15, 6.92. $C_{29}H_{54}N_2$. Calculated %: N 6.51

d) Tetramethylsuccinonitrile; m.p. 167.5-168° (the literature gives 169°); mixture test 168°; Yield 8.4g (55.5%).

e) Isobutyronitrile; yield 0.41 g (2.7%). This was determined by hydrolysis of the heptene fraction of the distillate from the reaction mixture. When the distillation of heptene was complete, the temperature of the oil bath was raised to 150°.

Products of the decomposition of 2,2'-azobis[2-methylpropionitrile] in α-methylstyrene. 2,2'-azobis[2-methylpropionitrile] (20 g) was decomposed at 80° in 288 g of α-methylstyrene. The main fraction obtained

* Tetramethylsuccinonitrile is not hydrolyzed under these conditions.

after removal of α-methylstyrene and tetramethylsuccinonitrile had b.p. 109-119° (2-3 mm), M 178, and iodine value 67.5; calculated for $C_{13}H_{15}N$: M 185, iodine value 135; calculated for $C_{13}H_{17}N$, M 187, iodine value 0.

Found %: N 7.94, 7.97. $C_{13}H_{15}N$. Calculated %: N 7.6. $C_{13}H_{17}N$. Calculated %: N 7.5

In view of the impossibility of separating the saturated and unsaturated components of this fraction by fractional distillation, the unsaturated component was isolated and characterized as the dibromide. For the establishment of the structure of the unsaturated component the ozonization method was employed. For the characterization of the saturated component, part of the fraction was first hydrogenated.

a) Bromination. The main fraction (2 g) was brominated in dilute carbon tetrachloride solution at 0°. The dibromide – white needles – had m.p. 71.5-72° (from methanol); yield 1.25 g.

Found %: Br 46.75, 45.65; N 4.07, 4.08. $C_{13}H_{15}NBr_2$. Calculated %: Br 45.40; N 4.06

b) Ozonolysis. The main fraction was refractionated, and a fraction of b.p. 129-132° (5 mm) was collected and used for the investigation: found – M 175, iodine value 120, N 7.61 and 7.29. The amount taken for ozonization was 2.07 g. Products found: 0.0415 g (13.5%) of formaldehyde, characterized as formaldimedone, m.p. 189° (the literature gives 189°); 0.22 g (48%) of formic acid, determined by Kucherov's reaction; 0.5 g of semicarbazone, m.p. 141-142.5° (from ethanol).

Found %: N 22.44, 23.15. $C_{13}H_{16}ON_4$. Calculated %: N 22.95

The carbazone isolated corresponds to the ketone $C_6H_5CO-CH_2-\underset{\displaystyle CN}{\overset{\displaystyle |}{C}}(CH_3)_2$.

On the basis of the ozonization results the unsaturated component must be assigned the structure (II).

c) Hydrogenation. Hydrogenation of 8.62 g of the fraction of b.p. 109-119° (2-3 mm) was carried out in alcoholic solution over palladium. The amount of hydrogen absorbed was 636 ml at 17° and 767 mm. After separation of catalyst and distillation of solvent the hydrogenation product remained as a pure substance, b.p. 100° (1.5 mm); $d_4^{18.5}$ 0.9425; $n_D^{18.5}$ 1.5000; found MR 58.37; M 184.5; calculated for $C_{13}H_{17}N$, MR 58.45; M 187.

Found %: C 82.91, 83.01; H 9.16, 9.14; N 7.71, 7.88. $C_{13}H_{17}N$. Calculated %: C 83.45; H 9.15; N 7.5

The structure of this compound corresponds to Formula (I). Comparison of data obtained in the investigation of the main fraction leads to the conclusion that it was an equimolecular mixture of (I) and (II), the yield of each being 26.5%. In the reaction mixture formed in the decomposition of the azo dinitrile in α-methylstyrene we found also: tetramethylsuccinonitrile – 5.75 g (34.7%), m.p. 168-169°; isobutyronitrile – 0.66 g (3.9%), determined by hydrolysis of the head fraction from the reaction mixture (b.p. 155-162°). Undistilled residue 6.8 g: found %: N 5.92, 6.17; M 309; iodine value 31. We did not succeed in separating the residue chromatographically on alumina. The resinous product probably contained a mixture of more complex saturated and unsaturated components of the types RA_2, R_2A_2, etc, e.g. $C_{22}H_{27}N$ (calculated: N 4.58%; M 305); $C_{22}H_{25}N$ (calculated: N 4.62 %; M 303; iodine value 84); $C_{26}H_{32}N_2$ (calculated: N 7.5%; M 372).

Products of the decomposition of 2,2'-azobis[2-methylpropionitrile] in isobutene. 2,2'-Azobis[2-methylpropionitrile] (20 g) was decomposed in 135 g of isobutene at 80°. Unchanged isobutene was distilled off, tetramethylsuccinonitrile was removed, and about 5 g of toluene was introduced into the reaction mixture. Isobutyronitrile was distilled off together with toluene. From the results of the hydrolysis of the toluene fraction

the yield of isobutyronitrile was 0.62 g (3.7%); the yield of tetramethylsuccinonitrile was 4.5 g (27%). Fractionation of the residue gave: Fraction I, b.p. 84-87° (1 mm) 2 g; Fraction II, b.p. 110-120° (1 mm) 7 g; Fraction III, b.p. 157-167° (2 mm) 4 g; distilled residue, 2 g. Fraction I was found to contain nitrogen (10.4%) and unsaturated compounds (iodine value 60), but no individual compounds were isolated from it. Fraction II solidified: m.p. 49-50° (from ethanol); found M 252; 245; calculated M 248; yield 23%.

Found %: C 77.78, 77.70; H 11.61, 11.52; N 11.58, 11.68. $C_{16}H_{28}N_2$ (RAAR). Calculated %: C 77.40; H 11.30; N 11.30

Fraction III: found M 286; calculated M 316; yield 15.5%

Found %: N 14.04, 13.96. $C_{20}H_{34}N_3$ (R_3A_2). Calculated %: N 13.3

Undistilled residue: found M 353; calculated M 373; yield 6.6%

Found %: N 11.52, 11.34. $C_{24}H_{42}N_3$ (R_3A_3). Calculated %: N 11.25

Gaseous products of the decomposition of 1-methyl-3-phenyltriazene in hydrocarbons. a) 1-Methyl-3-phenyltriazene (0.352 g) was decomposed in 2.5 g of 1-heptene (10 mole %) at 100°. The gas liberated amounted to 52 ml at 20° and 746 mm. The gas contained 13.5% (yield 15.8%) of methane and 86.5% (yield 72%) of nitrogen. b) Methylphenyltriazene (0.448 g) was decomposed in 3.3 g of heptane (10 mole %) at 100°. The gas liberated amounted to 100 ml at 20° and 759 mm. The gas contained 35.3% (yield 54.5%) of methane and 64.7% (yield 80.6%) of nitrogen. c) Methylphenyltriazene (0.501 g) was decomposed in 4.2 g of α-methylstyrene (10 mole %) at 100°. The gas liberated amounted to 61.2 ml at 20° and 767 mm. The gas consisted of pure nitrogen (yield 72%); no methane could be detected in the gas.

SUMMARY

1. A study was made of the products of the reactions of the free 1-cyano-1-methylethyl radical with 1-heptene, α-methylstyrene, and isobutene and also of the gaseous products of the decomposition of 1-methyl-3-phenyltriazene in heptane, 1-heptene, and α-methylstyrene.

2. It was shown that the presence of ethylenic double bonds leads to substantial reduction in the contribution made by the reaction of removal of a hydrogen atom from a hydrocarbon molecule by a free radical and, in certain cases, to complete suppression of this reaction (e.g. in the reaction between free methyl and α-methylstyrene).

3. The main products of the reactions of the free 1-cyano-1-methylethyl radical with 1-heptene and with isobutene are compounds of the type R — A — A — R, in which A is the hydrocarbon molecule. With α-methylstyrene reaction is mainly in the direction of disproportionation of free radicals with formation of R — A.

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NITRATION OF SACCHARIFICATION LIGNIN

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Little attention has been devoted to the nitration of lignin obtained by wood saccharification, and it was therefore of interest to study its behavior toward nitric acid. The nitration of native lignin and of isolated lignins obtained by hydrochloric acid and cuprammonium treatments has been studied by various investigators. The readiness with which lignin enters into combination with nitric acid and the good solubility of nitrolignins in dilute alkali enabled Coupier and Mellier [1] in 1852 to develop a method for the delignification of wood. It was later shown that the resulting nitrolignins, depending on the nitrating agent and the reaction conditions, vary not only in the amount of nitrogen bound, but also in the way in which it is bound. Thus, Kürschner [2], who subjected firwood to the action of nitric acid (sp.gr. 1.4) in alcoholic solution, isolated a nitrolignin containing 3.08-3.60% of nitrogen from the reaction mixture, and he considered that this nitrogen was bound in the form of nitro groups.

Lieser and Schaak [3] studied the nitration of pinewood, isolated lignins obtained by hydrochloric acid and cuprammonium treatments, and technical lignins of Tornesch-Scholler and Bergius with mixtures of nitric and sulfuric acids having various contents of water. Nitration proceeded readily and equilibrium was reached within 30 minutes. The nitration process was continued for two hours in all, and highly nitrated wood containing 12.70% of nitrogen was obtained. Nitrolignin was then isolated from the nitrowood; it contained up to 9% of nitrogen, and of this 6.0% was nitric-ester nitrogen. The total nitrogen content of nitrolignins obtained by the nitration of isolated lignins obtained by hydrochloric acid and cuprammonium treatments was 9.3-9.9% (nitric-ester nitrogen 5.6%), the yield being 34-120%. The technical lignins gave nitrolignins in 57-112% yield; they contained up to 7.9% of nitrogen, of which up to 4.4% was nitric-ester nitrogen. Yield and nitrogen content depended on the water content of the nitration mixture. The best results were obtained by nitration with a nitration mixture containing 15.9% of water.

Total nitrogen was determined by the Dumas method and nitric-ester nitrogen by the method of Schulze and Tiemann. According to Freudenberg and Dürr [4], nitration of lignin with oxides of nitrogen is accompanied by elimination of methoxy groups. There is an indication [5] that oxidation of native lignin results in the accumulation of carboxy groups.

We considered that study of the nitration of saccharification lignin and of the changes in its functional groups in the course of this process might give us a more complete picture of the character and properties of saccharification lignin. Saccharification lignin was nitrated with nitric acid (sp.gr. 1.52) and with nitric acid in presence of water-binding agents (sulfuric acid, phosphoric acid, and acetic anhydride). In the case of nitration with nitration mixture, we varied the amount of HNO_3 from 3.4 to 27%, the amount of H_2SO_4 from 60 to 91%, and the amount of water from 5 to 16%. The nitrolignins obtained were analyzed for nitrogen by the Dumas or Kjeldahl method, for nitric-ester nitrogen by the Schulze-Tiemann method, for methoxyl by the Kirpal-Bühn method, and for carboxyl by the calcium acetate method [6].

The nitrolignins obtained differed in yield, in nitrogen content, in the form in which nitrogen was bound, and in methoxyl and carboxyl contents. Thus, nitration of saccharification lignin with twenty times its amount of a 1 : 2.5 mixture of HNO_3 and H_2SO_4 containing 16% of water gave the highest yield of nitrolignin (97% of the initial amount of lignin): total nitrogen 7.01%; nitric-ester nitrogen 2.6%. There was simultaneous oxidation of the lignin with formation of up to 9.95% of carboxyls. The nitrolignins of highest nitrogen content (9.5%) were obtained by teatment of saccharification lignin with nitration mixtures of low water content with

preservation of the same relative amounts of nitric and sulfuric acids. Degradation of lignin with a drop in yield to 40% occurred under these conditions. For comparison purposes hydrochloric-acid lignin was nitrated with mixtures (1 : 2.5) of nitric and sulfuric acids containing 5 and 16% of water. The resulting nitrolignins had almost identical nitrogen contents (7.37 and 7.50%), but differed in yield and in methoxyl and carboxyl contents. The greater loss of methoxyls and higher degree of oxidation were suffered in the nitration of hydrochloric-acid lignin with the nitration mixture of low water content; the yields were 60% (5% water) and 114% (16% water).

Nitration of saccharification lignin with nitric acid (sp.gr. 1.52) at 14-16° for six hours was accompanied by less degradation of the lignin than nitration with the nitration mixture containing 24% of HNO_3, 60% of H_2SO_4, and 16% of H_2O for 4.5 hours and with a nitration mixture of low water content. Similar degradation was observed with nitric acid alone when the temperature was raised to 40°. These results give us reason to suppose that sulfuric acid does not lower the oxidizing effect of nitric acid.

In all such degradative nitrations of saccharification lignin, not only were water-insoluble nitrolignins obtained, but also water-soluble nitration products, which were isolated from the wash waters by acidification with dilute hydrochloric acid. Nitric-ester nitrogen was present in some of these to the extent of 1-2.1% but in others it was quite absent. Total nitrogen ranged from 3.9% to 8.00%. It must be pointed out that, unlike the water-insoluble nitrolignins, the water-soluble products contained up to 6% of nonester nitrogen. Of the nitrating agents that we used, the mixtures of nitric and phosphoric acids and of nitric acid and acetic anhydride were of interest. These agents give higher yields than nitration mixture (HNO_3, H_2SO_4, and H_2O) and nitric acid (sp.gr. 1.52). In an acetic anhydride medium the yield of nitration products was 110-120%, and in a phosphoric acid medium 113-123%. In phosphoric acid nitration was accompanied by more pronounced oxidation of lignin than in acetic anhydride.

Study of the functional groups COOH and OCH_3 in nitrated preparations showed that all the nitrating agents that we tried cause the loss of methoxyls and increase (from 4.5% to 12%) in the amount of carboxyls.

EXPERIMENTAL

In our experiments we used samples of saccharification and hydrochloric-acid lignin. Saccharification lignin obtained from the Leningrad Wood Saccharification Works was ground in a ball mill, extracted with hot water, extracted twice with dichloroethane, and dried – first in the air and then over phosphoric oxide. The composition of the hydrochloric-acid lignin was: C – 60.30%; H – 6.25%; OCH_3 – 15.10%; COOH – 0.68%. The composition of the saccharification lignin was: C – 62.78%; H – 5.79%; OCH_3 – 10.0%; COOH – 0.61%; carbohydrates – 19%.

Nitration of saccharification lignin was effected with nitration mixtures having various contents of nitric acid, sulfuric acid, and water. The amount of nitric acid was varied from 3.4 to 27%, the amount of sulfuric acid from 60 to 91%, and the amount of water from 5 to 16%. Nitration was carried out in a round-bottomed flask with stirring. Lignin was added to the nitration mixture in small portions over a period of 30 minutes. When the whole of the lignin had been added, the reaction mixture was stirred for one hour, after which it was transferred to a glass filter and filtered off at the pump. The precipitate was transferred in small portions into a large amount of ice water. The water-insoluble nitrolignin was filtered off and washed with cold water until the acid reaction disappeared. It was then dried – first in air, and then over phosphoric oxide in a vacuum desiccator.

In this way we obtained nitrolignins in the form of light-brown powders. All the samples were analyzed for total and nitric-ester nitrogen. The results are summarized in Tables 1 and 2, which show that all the nitrolignins contained 3-5% of nonester nitrogen. The results of experiments on the nitration of hydrochloric-acid lignin with mixtures of nitric and sulfuric acids (1 : 2.5) containing 5% and 16% water are given in Table 3.

In the treatment of hydrochloric-acid lignin with nitration mixture containing 16% of water the results were almost the same as with saccharification lignin. With nitration mixtures of low water content we obtained nitrolignins of lower nitrogen content (7.5%) than in the case of saccharification lignin treated with the same reagent (9.5%).

TABLE 1

Nitration of Saccharification Lignin with Nitration Mixture (relative amounts of lignin and nitrating agent 1 : 10).

Experiment	Ratio HNO_3 : H_2SO_4	H_2O content of nitration mixture (%)	Reaction temperature (°C)	Yield of water-insoluble nitrolignin (% on original amount of lignin)	Nitrogen content (%)		
					Total	Nitric-ester	Difference
1	1 : 25	6	15—20	79.3	3.74	0	3.74
2	1 : 25	6	15—20	73.8	3.71	0	3.71
3	1 : 25	15	15	85.32	2.70	0	2.70
4	1 : 25	15	12—15	92.00	2.80	0	2.80
5	1 : 15	15	12—15	88.30	3.95	0	3.95
6	1 : 15	15	12—15	88.70	3.95	0	3.95
7	1 : 10,8	15	10—12	55.50	4.08	0	4.08
8	1 : 10,8	15	10—12	59.20	4.27	0	4.27
9	1 : 2,5	16	10—12	41.00	5.77	0.65	5.12
10	1 : 2,5	16	10—12	49.10	5.74	0.85	4.89

TABLE 2

Nitration of Saccharification Lignin with Nitration Mixture (relative amounts of lignin and nitrating agent 1 : 20).

Experiment	Ratio HNO_3 : H_2SO_4	H_2O content of nitration mixture (%)	Reaction Temperature (°C)	Yield of water-insoluble nitrolignin (% on original amount of lignin)	Nitrogen content (%)		
					Total	Nitric-ester	Difference
11	1 : 2.5	16	10—12	96.00	7.01	2.60	4.41
12	1 : 2.5	16	10—12	95.40	6.80	2.60	4.20
13	1 : 2.5	16	—4	96.40	6.90	2.06	4.84
14	1 : 2.5	7	10—12	44.00	9.00	4.99	4.01
15	1 : 2.5	5	10—12	41.60	9.36	6.02	3.34
16	1 : 2.5	5	10—12	40.00	9.60	6.70	2.90

TABLE 3

Nitration of Hydrochloric-acid Lignin with Nitration Mixture at 10-14° (relative amounts of lignin and nitrating agent 1 : 20).

Expt.	Ratio HNO_3 : H_2SO_4	H_2O content of nitration mixture (%)	Yield of water-insoluble nitrolignin (% on original amount of lignin)	Nitrogen content (%)		
				Total	Nitric-ester	Difference
1	1:2.5	16	114.4	7.50	—	—
2	1:2.5	5	60.85	7.37	—	—

TABLE 4

Nitration of Saccharification Lignin with Nitric Acid (sp.gr 1.52) (relative amounts of lignin and nitrating agent 1 : 14).

Experiment	Reaction temperature (°C)		Duration of nitration (minutes)	Yield of water-insoluble nitrolignin (% on original amount of lignin)	Nitrogen content (%)		
	During addition of lignin	After addition of lignin			Total	Nitric-ester	Difference
43	—10	14—16	360	68.73	8.41	4.40	4.01
44	—10	14—16	360	60.0	8.41	4.72	3.69
29	—10	40	70	58.73	9.40	5.40	4.00
33	—10	40	70	60.01	9.24	4.64	4.60
30	—10	40	120	33.76	10.20	7.27	2.93
32	—10	40	120	33.25	10.11	6.80	3.31
40	—10	40	240	39.27	9.69	5.79	3.90
41	—10	40	240	34.30	9.50	6.07	3.43

TABLE 5

Water-soluble Nitrolignins.

Experiment	Ratio HNO_3 : H_2SO_4	H_2O content of nitration mixture (%)	Reaction temperature (°C)	Modulus of bath	Yield of nitrolignin (%on original amount of lignin)	Nitrogen content (%)		
						Total	Nitric-ester	Difference
5	1 : 15	15	12—15	1 : 10	17.80	3.90	0	3.90
7	1 : 10.8	15	10—12	1 : 10	24.50	4.06	0	4.06
8	1 : 10.8	15	10—12	1 : 10	22.40	4.80	0	4.80
9	1 : 2.5	16	10—12	1 : 10	24.30	5.49	0	5.49
10	1 : 2.5	16	10—12	1 : 10	25.20	5.31	0	5.31
15	1 : 2.5	5	10—12	1 : 20	30.10	6.57	1.20	5.37
16	1 : 2.5	5	10—12	1 : 20	30.50	6.35	1.05	5.30
17	1 : 2.5	5	10—12	1 : 20	30.50	6.61	1.34	5.27

TABLE 6

Water-soluble Nitrolignins obtained by Nitration with Nitric Acid (relative amounts of lignin and nitrating agent 1 : 14).

Experiment	Reaction temperature (°C)		Duration of nitration (minutes)	Yield of nitrolignin (%on original amount of lignin)	Nitrogen content (%)		
	During addition of lignin	After addition of lignin			Total	Nitric-ester	Difference
29	—10	40	70	13,97	7.45	2,10	5.35
33	—10	40	70	19,90	6.72	0,91	5.81
30	—10	40	120	37,09	8.00	2,03	5.97
32	—10	40	120	42,04	6.78	1,17	5.61
40	—10	40	240	24,81	6.25	1,19	5.06
41	—10	40	240	29,13	6.57	0.81	5.76
43	—10	14—16	360	18,93	7.50	—	—
44	—10	14—16	360	26,2	7.40	—	—

Experiments on the nitration of saccharification lignin with nitric acid (sp.gr. 1.52) were carried out at 14-16° and at 40° for various times. The results are given in Table 4, which shows that increase in the duration of reaction beyond two hours leads to a fall in the yield of nitration product. Our experiments showed that wash waters from highly degraded nitrolignins (reagents: nitration mixture and nitric acid) contained water-soluble nitrolignins. These were isolated from the wash waters by acidification with dilute hydrochloric acid. The precipitates were filtered off and dried – first in the air, then over alkali in a vacuum desiccator until hydrochloric acid was removed completely, and finally over phosphoric oxide. The nitration products obtained were analyzed for total nitrogen and nitric-ester nitrogen. The results of the experiments are given in Tables 5 and 6.

TABLE 7

Nitration of Saccharification Lignin with Nitric Acid (sp.gr. 1.52) in Media of Acetic Anhydride and of Phosphoric Acid (relative amounts of lignin and nitrating agent 1 : 20).

Experiment	Nitrating agent (%)	Reaction temperature (°C)		Duration of nitration (minutes)	Yield of water-insoluble nitrolignin (% on original amount of lignin)	Nitrogen content (%)		
		During addition of lignin	After addition of lignin			Total	Nitric-ester	Difference
1	HNO_3—20 $(CH_3CO)_2O$—80	10	10	105	110.3	6.82	3.04	3.78
2	Ditto	10	10	120	120.0	7.63	3.16	4.47
3	"	10	10	120	120.0	7.60	3.11	4.49
4	HNO_3—20 H_3PO_4—80	20	20	120	123.0	8.02	2.80	5.22
5	Ditto	20	20	120	113.4	7.75	3.10	4.65

TABLE 8

Effect of Composition of Nitrating Agent on Contents of Functional Groups in Nitrolignins.

Experiment	Lignin*	Nitrating agent (%)	Content (%) of		
			Nitrogen	COOH groups	OCH_3 groups
1	Hydrochloric-acid	HNO_3 —27 H_2SO_4—68 H_2O — 5	7.50	11.98	3.80
2		HNO_3 —24 H_2SO_4—60 H_2O —16	7.37	8.42	5.50
3	Saccharification	HNO_3 —24 H_2SO_4—60 H_2O —16	7.20	9.95	3.01
4	"	HNO_3 — 3 H_2SO_4—91 H_2O — 6	3.72	8.70	3.00
5	"	HNO_3 — 7 H_2SO_4—77 H_2O —16	4.27	10.04	3.70
6	"	HNO_3 . .	9.50	9.70	3.00
7	"	HNO_3 —20 H_3PO_4—80	8.02	6.71	2.33
8	"	HNO_3 —20 $(CH_3CO)_2O$—80	7.60	4.51	3.25

* COOH content: HCl- lignin 0.68%, saccharification lignin 0.61%. OCH_3 content: HCl- lignin 15.5%, saccharification lignin 10.0%.

We studied also the nitration of saccharification lignin with nitric acid in media of phosphoric acid and of acetic anhydride (Table 7). The results of determinations of functional groups in water-insoluble nitrolignins are given in Table 8.

SUMMARY

1. A study was made of the nitration of saccharification lignin with a mixture of nitric and sulfuric acids having various water contents (5-16%), with a mixture of nitric acid and crystalline phosphoric acid, with nitric acid in a medium of acetic anhydride, and with nitric acid of sp.gr. 1.52. The highest yields of nitrolignins were obtained by treatment of lignin with mixtures of nitric and phosphoric acids and of nitric acid and acetic anhydride. The products had total nitrogen contents of 7.50-8.00%.

2. It was found that nitration of saccharification lignin with nitration mixtures of low water content at 10-15° or with pure nitric acid at 40° resulted in the highest uptake of nitrogen in the nitric-ester form (6.5%), but was associated with degradation of the lignin. Under all conditions nitration of the nucleus was predominant. If we assume that the structural units of lignin are derivatives of 4-propylguaiacol and take account of the carbohydrate content of the lignin, then the content of nonester nitrogen corresponds to almost one nitro group to each structural unit of the lignin molecule.

3. A study of the functional groups of nitrolignins (COOH, OCH_3) showed that, under all the conditions which we tried, the nitration of saccharification lignin results in reduction in the number of methoxy groups and considerable increase in the number of carboxy groups.

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BRIEF COMMUNICATIONS

THERMAL TRANSFORMATIONS OF TETRACHLOROETHYLENE UNDER PRESSURE

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We have described experiments [1] in which we tried to bring about the polymerization of tetrachloroethylene at high temperatures under pressures of up to 30,000 atm. We did not succeed in polymerizing tetrachloroethylene under these conditions, but we found that, at 300-350° under superhigh presures, tetrachloroethylene undergoes thermal transformations with formation mainly of hexachloroethane and hexachlorobenzene, and also some resin and a small amount of a heavy liquid which came over with the hexachloroethane.

EXPERIMENTAL

It was of interest to investigate this process at lower pressures. The experiments were carried out in a steel ampoule, about 21 ml in volume, which was filled completely with tetrachloroethylene and placed in an electric tube furnace. When the temperature of the experiment (300°) had been established as indicated by thermocouples inside and outside the ampoule (the readings agreed within ± 2°), the ampoule was maintained at that temperature for the necessary time and the furnace was then cooled.

The experiments showed that under these conditions tetrachloroethylene is very slowly converted into hexachloroethane and hexachlorobutadiene. Thus, after reaction for 56 hours 28% of C_2Cl_6 and 28% of C_4Cl_6 were found. Further investigation showed that these thermal transformations of tetrachloroethylene are considerably accelerated by increase in pressure. However, C_4Cl_6 then underwent further thermal transformations. On the basis of an analysis of the results we are able to suggest the following radical-chain reaction mechanism:

$$2C_2Cl_4 \rightarrow \dot{C}_2Cl_3 + \dot{C}_2Cl_5 \quad (1) \quad \text{(initiation)}$$

$$\left.\begin{array}{l} \dot{C}_2Cl_3 + C_2Cl_4 \rightarrow CCl_2 = CCl - CCl_2 - \dot{C}Cl_2 \quad (2) \\ CCl_2 = CCl - CCl_2 - \dot{C}Cl_2 + C_2Cl_4 \rightarrow C_4Cl_6 + \dot{C}_2Cl_5 \quad (3) \\ \dot{C}_2Cl_5 + C_2Cl_4 \rightarrow C_2Cl_6 + \dot{C}_2Cl_3 \quad (4) \end{array}\right\} \text{(propagation)}$$

$$\left.\begin{array}{l} 2\dot{C}_2Cl_3 \rightarrow C_4Cl_6 \quad (5) \\ 2\dot{C}_2Cl_5 \rightarrow C_2Cl_4 + C_2Cl_6 \quad (6) \end{array}\right\} \text{(termination)}$$

In resolving the question of the form of the equation for the reaction of chain initiation, we made a theoretical comparison of the rate of Reaction (1) and the rate of unimolecular decomposition in accordance with the equation

$$C_2Cl_4 \rightarrow \dot{C}_2Cl_3 + \dot{C}l$$

and we came to the conclusion that under our conditions Reaction (1) is the more probable [2]. Reaction (3) is analogous to that proposed by Voevodsky [3] in an analysis of the mechanism of the thermal decomposition of unsaturated hydrocarbons.

We did not observe chain-termination reactions with formation of octachlorobutene ($\dot{C}_2Cl_3 + \dot{C}_2Cl_5 \rightarrow C_4Cl_8$) and decachlorobutane ($2\dot{C}_2Cl_5 \rightarrow C_4Cl_{10}$). It is known [4] that at 220-250° octachlorobutene decomposes smoothly into two molecules of tetrachloroethylene and that above 200° decachlorobutane decomposes into

tetrachloroethylene and hexachloroethane. Under the above-indicated conditions the thermal transformations of tetrachloroethylene proceed in the liquid phase. We made approximate determinations of the critical temperature and critical density of tetrachloroethylene by the disappearing-meniscus method. The critical temperature of tetrachloroethylene was found to be 338 ± 2° and its critical density 0.5-0.6 g/cc.

We take this opportunity to express our sincere thanks to I. R. Krichevsky for making it possible for us to make determinations of critical temperature and pressure and to N. E. Khazanov for valuable directions and help in carrying them out.

SUMMARY

1. It was found that thermal transformations of tetrachloroethylene under pressure can lead to the formation of hexachlorobutadiene and hexachloroethane.

2. A radical-chain mechanism is proposed for this reaction.

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• [See C. B. translation].

USE OF THE KINETIC METHOD FOR THE DETERMINATION OF ORDER OF REACTION

M. B. Neiman

The problem of determining the order of a reaction by which an intermediate product is consumed in a complex reaction could not be solved by any known method until recently. The kinetic method of applying labeled atoms, which we have developed [1], enables this problem to be solved in certain cases. First, we shall analyze the application of the method for the determination of the order of the reaction by which the starting substance is consumed, i.e.

$$A \xrightarrow[n]{w} B \rightarrow \ldots$$

If the order of reaction is n, then

$$-\frac{dA}{dt} = kA^n. \tag{1}$$

If we add a little labeled A, then the starting substance will have a specific activity α, which will be constant throughout the whole process.

Multiplying both sides of Equation (1) by α, we obtain:

$$-\alpha\frac{dA}{dt} = kA^n\alpha. \tag{2}$$

The value of I, the activity of A, is given by the equation

$$I = \alpha A. \tag{3}$$

Substituting the value of I given by (3) into (2), we obtain

$$-\frac{dI}{dt} = kA^{n-1}I. \tag{4}$$

It follows from this that

$$-\frac{d\ln I}{dt} = kA^{n-1}. \tag{5}$$

If I is determined at different times during the reaction, then with the aid of Equation (5) it is possible to calculate n and so determine the order of the reaction. In the case examined the value of n can be determined also by the van't Hoff, Ostwald, and other classical methods.

The matter is different when A is an intermediate product in a complex reaction:

$$\ldots \rightarrow X \xrightarrow{w_1} A \xrightarrow{w_2} Y \rightarrow \ldots$$

For this case:

$$\frac{dA}{dt} = w_1 - w_2. \tag{6}$$

In order to determine the order of reaction it is necessary to know the rate w_2 at which A is consumed, and for this it is necessary to know the value of w_1. This problem, which could not be solved by earlier methods, can be solved with the aid of the equation of the kinetic method:

$$-\frac{d\alpha}{dt} = \frac{\alpha w_1}{A}. \tag{7}$$

Here α is the specific activity of A, which alters during the reaction.

Having found the value of w_1 from Equation (7) and substituted it in Equation (6), we obtain:

$$w_2 = -A\frac{d\ln\alpha}{dt} - \frac{dA}{dt} = kA^n. \tag{8}$$

Multiplying Equation (8) by α we obtain:

$$-A\frac{d\alpha}{dt} - \alpha\frac{dA}{dt} = kA^n\alpha. \tag{9}$$

Replacing αA by the total activity I in accordance with Equation (3), we obtain:

$$-\frac{d\ln I}{dt} = kA^{n-1}. \tag{10}$$

Hence, for an intermediate product in a complex reaction we obtain exactly the same equation as Equation (5) for the starting substance.

If we determine the value of I for A at various times during the reaction, we can calculate the order of reaction n. For this purpose it is simplest to plot the experimental results on a graph of log I against t. If the experimental points fit closely to a straight line, then d log I/ dt is constant and the order of reaction $n = 1$. The determination of order of reaction for reversible processes is a more complex problem which can also be solved with the aid of the kinetic method.

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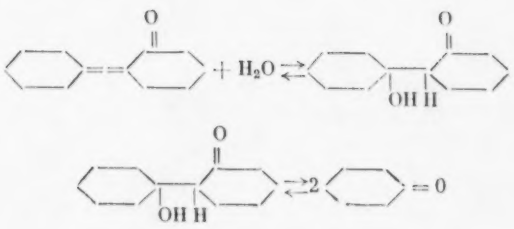
HYDROLYTIC SCISSION OF 2-CYCLOHEXYLIDENECYCLOHEXANONE INTO CYCLOHEXANONE

L. Kh. Freidlin and V. Z. Sharf

We recently showed that in the vapor phase in presence of tricalcium diphosphate, as also in the liquid phase in presence of H^+ and OH^- ions, the hydrolytic scission of mesityl oxide into acetone passes through a hydration stage which limits the overall rate of the process. It was considered to be of interest to study the hydrolytic scission of another α, β-unsaturated ketone, 2-cyclohexylidenecyclohexanone, which probably proceeds in accordance with the scheme:



This reaction has not been studied previously: there is a patent which states that cyclohexanone can be prepared from 2-cyclohexylidenecyclohexanone by heating it with water under pressure, best with the addition of 0.2% of benzoic, adipic, or boric acid [1]; the yield of cyclohexanone was not indicated. When our work was complete and was being prepared for publication, a second patent appeared in which it was recommended that the reaction be carried out in the liquid phase under pressure in presence of alkaline catalysts [2].

Since the degree of conjugation diminishes from ketones of the type RCH = CHCOR through ketones of the type RCR = CHCOR, to trialkylvinyl ketones RCR =CRCOR [3], it would be expected that the hydrolytic scission of 2-cyclohexylidenecyclohexanone would be more difficult than that of mesityl oxide. Our results confirm this view.

EXPERIMENTAL

Analytical procedure. The cyclohexanone formed in the reaction was distilled off through a 25-plate column in the form of an azeotrope with water, b.p. 96-97°. It was then analyzed by the oxime method in presence of Methyl orange. 2-Cyclohexylidenecyclohexanone was prepared by condensation of cyclohexanone in presence of 60% sulfuric acid [4] and had b.p. 134-136° (11 mm) and n_D^{20} 1.5077, which are in accord with the literature [5].

Vapor-phase scission of 2-cyclohexylidenecyclohexanone. Reaction was carried out in a flow apparatus with 20 ml of catalyst. In each experiment 10 ml of ketone and a definite amount of water were passed through the catalyst. Tricalcium diphosphate was prepared from calcium chloride and ammonium phosphate. The alkaline catalyst was prepared by impregnating alumina with 10% aqueous sodium carbonate. In experiments with calcium phosphate the highest yield of cyclohexanone in a single passage was 32% and was obtained at 400° with a time of contact of ten seconds. At 460° the yield was only 8.4%. The products of side reactions

were not studied. With the Na_2CO_3 — Al_2O_3 catalyst the highest yield of cyclohexanone was 48.0% (300° for 10 seconds). At 350° the yield was reduced to 35%.

Liquid-phase scission of 2-cyclohexylidenecyclohexanone. It would be expected that this ketone would react with water much less readily than mesityl oxide. It is in fact found that, when treated at the boil with 2% sulfuric acid or 2% sodium hydroxide solution for six hours, 2-cyclohexylidenecyclohexanone yields only traces of cyclohexanone.

Experiments were then carried out at higher temperatures and pressures (table).

TABLE

Liquid-phase Hydrolytic Scission of 2-Cyclohexylidenecyclohexanone into Cyclohexanone.

Experiment	Water : 2-cyclohexylidenecyclohexanone ratio		Catalyst and concentration in aqueous solution (% by weight)	Reaction temperature (°C)	Pressure (atm)	Duration of experiment (hours)	Yield of cyclohexanone (%)
	By weight	Molar					
1	5	50	None	230	26	4	2
2	5	50	NaOH, 2	300	85	4	62
3	5	50	NaOH, 2	200	16	4	68
4*	5	50	NaOH, 2	230	26	2	74
5	5	50	NaOH, 2	230	26	1	75
6	5	50	NaOH, 2	230	26	0.5	75
7	5	50	NaOH, 2	200	16	0.5	33
8	5	50	NaOH, 2	230	26	0.5	83
9	5	50	NaOH, 2	260	46	0.5	80
10	2	20	NaOH, 2	250	40	0.5	91
11	5	50	NaOH, 1	250	40	0.5	80
12	5	50	NaOH, 0.5	250	40	0.5	84
13	5	50	NaOH, 0.1	250	40	0.5	6
14	1	10	NaOH, 0.5	250	40	0.5	85
15	5	50	KOH, 0.5	250	40	0.5	86
16	5	50	Na_2CO_3, 0.5	250	40	0.5	84
17	5	50	$Ca(OH)_2$, 0.5	250	40	0.5	8
18	5	50	H_3BO_3, 0.5	250	40	0.5	2

* From the fourth experiment onward reaction was carried out with rotation of the autoclave.

An aqueous solution of the catalyst was introduced together with the ketone into an autoclave. The autoclave was closed and blown out with nitrogen; the heating and the rotation mechanism were switched on. In absence of catalyst the conversion into cyclohexane was only 2%. In presence of sodium hydroxide (2%) the yield of cyclohexanone attained 80-90%. The optimum temperature was found to be 230-260°; at 300° side reactions already appeared to be occurring. The results of Experiment 4 showed that rotation of the autoclave had no effect on the yield of cyclohexanone. Reduction of the duration of reaction from four hours to 30 minutes did not reduce the yield of cyclohexanone (Experiments 4-6). Reduction of the concentration of the alkali solution to 0.5% and the relative weights of water and 2-cyclohexylidenecyclohexanone to 5 : 1 did not lower the yield of cyclohexanone (Experiments 10-14). The use of a 0.1% alkali solution led to a sharp fall in the yield of cyclohexanone to 6%. With potassium hydroxide and sodium carbonate under optimum conditions we obtained the same yields of cyclohexanone as with sodium hydroxide (Experiments 15 and 16).

Experiments with a continuous apparatus. The autoclave experiments show that reaction is almost complete in 30 minutes and can be carried out without mechanical agitation. This method can be used for the preparation of cyclohexanone from 2-cyclohexylidenecyclohexanone, which is obtained in considerable amount as a byproduct of the dehydrogenation of cyclohexanol in the manufacture of caprolactam. In this connection we

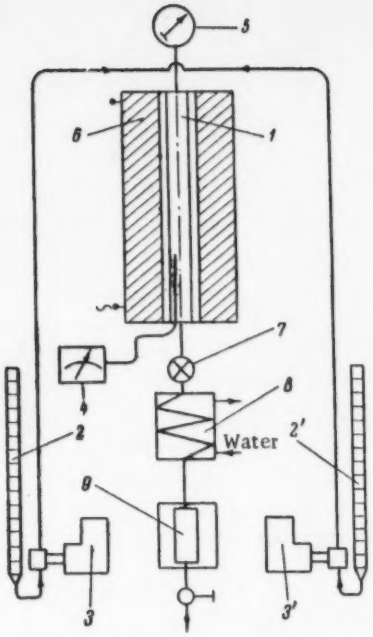


Fig. 1.

carried out experiments with a continuous apparatus (Fig. 1). 2-Cyclohexylidenecyclohexanone and 0.5% sodium hydroxide solution were drawn by the hydraulic pumps (3 and 3') from two burets (2 and 2') and passed under pressure through steel capillaries to the upper part of the reactor (1), diameter 20 mm and length 400 mm. The temperature was measured with a thermocouple (4) inserted in the reactor wall. The reactor was furnished with a manometer (5) and a furnace (6), which was thermostatically controlled. The reaction mixture left the reactor continuously through a finely controlled valve (7) and a cooling coil (8); it was collected in the receiver (9). In this way continuous feed of reactants and withdrawal of reaction products were effected. The experiments were carried out at 260° and the relative weights of ketone, water, and alkali were 1 : 1 : 0.05. The average period during which the reactants were in the reactor was 20, 40 or 60 minutes. The yield of cyclohexanone was high in all the experiments and varied over the range 80-90%.

SUMMARY

1. An investigation was made of the effects of type of catalyst, temperature, and other factors in the reaction of hydrolytic scission of 2-cyclohexylidenecyclohexanone into cyclohexanone.

2. It was shown that, in accordance with the lower degree of conjugation of this ketone, its scission proceeds less readily than that of mesityl oxide. When the reaction was carried out under pressure in presence of an alkaline catalyst, the conversion into cyclohexanone attained 80-90%. A similar result was obtained in a continuous apparatus.

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• [See C. B. translation].

OPTICAL INVESTIGATION OF INTERMOLECULAR ACTION BETWEEN Si AND Cl

M. I. Batuev, V. A. Ponomarenko, A. D. Matveeva, and A. D. Snegova

In a previous paper [1] on the optical (Raman spectrum) investigation of the factors determining the β-decomposition of β-halo organosilicon compounds, we concluded that a substantial part is played in β-decomposition by intermolecular forces due to interaction between Si and Cl. However, we did not obtain direct confirmation of this intermolecular action in that investigation [1]. It is not impossible to obtain such confirmation by optical methods, as is shown by the optical manifestation of a particular case of intermolecular action, namely, hydrogen bonding. This is clearly shown in, for example, the spectra of the hydroxy group of acetic acid. In the gas phase (isolated molecules) the hydroxyl frequency is 3578 cm^{-1} and is represented by a sharply defined line in the Raman spectrum; in the liquid phase the hydroxyl of acetic acid takes part in a hydrogen bond with the aid of which straight-chain and cyclic complexes are formed, and its spectrum is no longer characterized by a single line, but by a band, displaced in the direction of the longer waves and about 900 cm^{-1} in width (~ 2700-3600 cm^{-1})•.

The hydrogen bond, of course, is a very specific case of intermolecular action. However, the case under examination has something in common with the hydrogen bond – the disturbing effect of a chlorine atom of another molecule on the Si – Cl and Si – C bonds of the given molecule and the disturbing effect of a silicon atom on a C – Cl in another molecule (see (I) and (II)), which is analogous in a hydrogen bond to the disturbing effect of an oxygen in one molecule on a hydroxyl in another. In our case and in the case of the hydrogen bond, the disturbing effects are of course different. However, on the basis of the common behavior in the two cases we may expect that there will be some blurring of the vibration frequencies of Si – Cl, C – Cl, and Si – C bonds in the case of the β-halo organosilicon compound that we have investigated, $Cl_3Si - CH_2CH_2 - Cl$, which is what we have actually found.

The action of a chlorine atom of one molecule on the silicon atom of a silyl group of another molecule constitutes a tendency for the chloro and silyl groups to be torn away with formation of $SiCl_4$:

$$\begin{array}{l} Cl_3Si - CH_2CH_2 - Cl \\ \vdots \qquad\qquad\quad \vdots \\ Cl - CH_2CH_2 - SiCl_3 \\ \text{(I)} \end{array} \rightarrow 2CH_2 = CH_2 + 2SiCl_4,$$

$$\begin{array}{l} \qquad\qquad\quad Cl_3Si - CH_2CH_2 - Cl \\ \qquad\qquad\quad \vdots \\ Cl_3Si - CH_2CH_2 - Cl \\ \qquad\quad \text{(II)} \end{array} \rightarrow CH_2 = CH_2 + SiCl_4.$$

The tendency for the rupture of the C – Cl bond implies that it is weakened to some extent, and this weakening is bound to aid in the blurring of its vibration frequency in the low-frequency region. The frequency assigned to the vibration, 722 cm^{-1} [1], is indeed blurred on its low-frequency side (Fig. Spectrum 1). The tendency for the silyl group to unite with a chlorine atom with formation of $SiCl_4$ means that there is a tendency

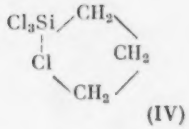
• See the photograph of the spectra of the hydroxy group of acetic acid in the gas and liquid phases in [2].

for the lowering of the frequency of the symmetrical vibration of Si – Cl of the silyl group (470 cm^{-1}), since the corresponding vibration in $SiCl_4$ has a much lower frequency (424 cm^{-1}).* This is actually observed; the diffuseness of the group should also favor the blurring of the intense line at 470 cm^{-1} (Fig., Spectrum 1) in the low-frequency direction (it has the form of a band centered on 448 cm^{-1}).

For substances close in composition to the β-halo compound investigated, but not showing imtermolecular actions of the type under discussion, there is not the slightest sign of diffuseness on the low-frequency side of the corresponding lines (Spectra 2-6 on the Fig.).**

At low concentration in cyclohexane solution, the diffuseness of these lines in the direction of lower frequencies disappears as the complexes break down.

In [1] we showed that the γ-halo compound $Cl_3Si-CH_2CH_2CH_2-Cl$ (III) decomposes under suitable conditions with formation of $SiCl_4$ and cyclopropane, not propene. In this connection we pointed out the possibility of the existence of this γ-halo compound not only in the form (III), but also in the form (IV), which favors the formation of cyclopropane:



(IV)

The large number of lines in the spectrum of the γ-halo compound, which greatly exceeds the number theoretically possible, and the presence of double, broadened, and merging lines, etc. indicates that, in the liquid state, this compound exists as a mixture of two forms, (III) and (IV), which may be regarded as being dissolved in each other. The form (III), when dissolved in the form (IV) does not form complexes of the type (I) and (II), which could give rise to propene by γ-decomposition. However, solution of form (IV) in form (III) does not result in rupture of the Si...Cl intermolecular bond, the behavior being analogous to the case of the intermolecular hydrogen bond [4]. This bond is represented in the spectrum as a blurring of the frequency of the symmetrical Si – Cl vibration of the form (IV): the blurring of the intense line at 471 cm^{-1} on its low-frequency side gives it the form of a band centered on 457 cm^{-1}, but it is somewhat narrower than in the case of the intermolecular Si...Cl bond (compare the case of the intermolecular hydrogen bond [4]). In the form (III) the frequency of the symmetrical Si – Cl vibration at 490 cm^{-1} is not blurred; as we have stated, when dissolved in form (IV), form (III) does not form complexes. The C – Cl frequency (712 cm^{-1}) is also blurred.

Raman Spectrum of $Cl_3Si-CH_2CH_2CH_2-Cl$***

Δνсм⁻¹: 92(3*), 108(3*), 122(3*), 170(7), 208(4ш), 231(3ш), 270(2 дв.), 298(7), 369(0), 402(7), 457(2*), 471(6*), 490(9), 562(3*), 574(3*), 591(3*), 657(6ш), 712(5ш), 753(3ш), 786(4ш), 834(0), 860(2 дв), 893(0), 915(3), 1002(3), 1030(2*), 1042(2*), 1053(2*), 1101(1), 1118(2*), 1175(2*), 1233(3), 1272(4), 1299(3), 1350(3ш, дв), 1394(4ш), 1421(1), 1444(7), 2833(0*), 2850(3*), 2871(3*), 2896(9*), 2921(7*дв), 2945(1*), 2959(7*), 3000(4дв).

In the very broad wing of the Rayleigh band, which extends to about 250 cm^{-1}, are to be found the intermolecular vibrations in Si...Cl bonds in complexes of the type (I) and (II); they are analogous to those found for intermolecular vibrations in complexes formed with a hydrogen bond [5].

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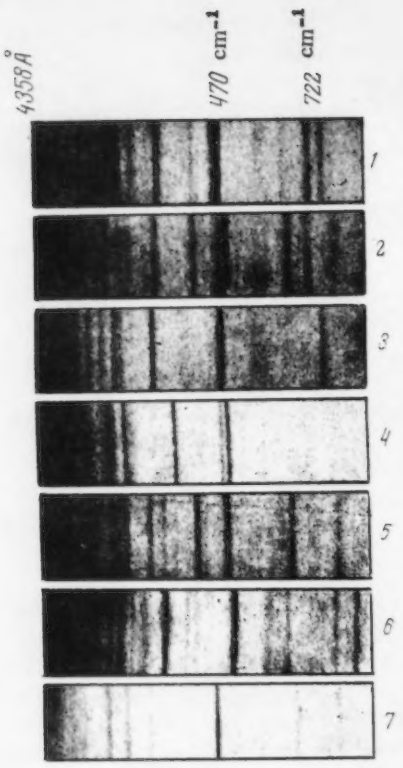
* We do not discuss the antisymmetrical vibration of the silyl group and the Si – Cl vibrations owing to their low intensities and closeness to other frequencies.

** For the spectra of Compounds 1-6 (Figure) see [3]; for that of Compound 7 see end of this paper.

*** The spectrum was determined with an ISP-51 three-prism spectrograph with central camera and exciting radiation from the mercury line 4358 A. In parentheses there are figures indicating intensities, b indicating broad line, db indicating double line, and asterisks indicating that the line has a background in common with neighboring lines indicated by the same number of asterisks. [ш is the equivalent of 'b', and Ш ≡ 'db' in the Raman spectrum – Publisher].



Raman spectra (exciting line 4358 A): 1) $Cl_3Si - CH_2CH_2 - Cl$; 2) $Cl_3Si - CH_2CH_2CH_2 - Cl$; 3) $Cl_3Si - CH_2CH_2SiCl_3$; 4) $Cl_3Si - CH_2CH_2 - CH_3$; 5) $Cl_3Si - CH(Cl) - CH_3$; 6) $Cl_3 - CH(Cl)CH_2 - SiCl_3$; 7) $Cl_3Si - CH_2 - Cl$.

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SUMMARY

The intermolecular action through Si...Cl bonds in $Cl_3Si - CH_2CH_2 - Cl$ and the intramolecular action through Si...Cl in $Cl_3Si - CH_2CH_2CH_2 - Cl$ were detected in the liquid phase by optical (Raman spectrum) analysis.

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* [See C. B. translation].

TRIALKYLFLUOROSILANES

M. G. Voronkov

The simplest method of preparing trialkylfluorosilanes is based on the splitting of hexaalkyldisiloxanes with hydrogen fluoride in presence of a water-eliminating agent (generally sulfuric acid):

$$R_3SiOSiR_3 + 2HF \xrightarrow{-H_2O} 2R_3SiF.$$

This reaction has been carried out by treating solutions of hexaalkyldisiloxanes in sulfuric acid with anhydrous hydrogen fluoride [1] or with ammonium fluoride, which gives hydrogen fluoride with the sulfuric acid [2]

TABLE

Trialkylfluorosilanes R_3SiF.

R	B.p.(°C at 760 mm)	d_4^{20}	d_4^{25}	n_D^{20}	F found (%)	F calculated (%)	Yield (%)
CH_3	16.4	0.7946*	—	—	20.50; 20.42	20.61	85
C_2H_5**	109.4	0.8360	0.8326	1.3900	14.15; 14.17	14.15	85
n-C_3H_7	174.5	0.8384	0.8351	1.4117	10.79; 10.81	10.77	86
n-C_4H_8***	225.3	0.8404	0.8372	1.4238	8.71; 8.72	8.70	88

* d_4^0

** СКРΔ$^\nu$ $см^{-1}$: 235 (1), 246 (1), 306 (1 д), 395 (1 д), 480 (1д), 572 (10), 585 (5), 632 (1), 679 (1д), 744 (1пд), 801 (о), 832 (1д), 973 (5д), 1008 (4д), 1111 (1д), 1226 (2), 1239 (2), 1411 (5д), 1463 (8п), 2386 (15п), 2895 (4), 2944 (2), 2966 (10).

*** СКРΔ$^\nu$ $см^{-1}$: 273 (3п), 410 (2), 610 (3), 650 (2п), 746 (1), 790 (1), 835 (2), 854 (3), 888 (6), 963 (4), 1026 (1), 1048 (6), 1080 (6), 1137 (0), 1194 (5), 1289 (4), 1305 (4), 1338 (3), 1408 (4), 1446 (8п), 1456 (3), 2660 (оп), 2695 (оп), 2733 (2), 2850 (2п), 2881 (15п), 2910 (4п), 2938 (8), 2960 (10п).

[СКР = 'Raman spectrum'; Ш = 'b'; Д = 'd'. – Publisher].

We synthesized a series of trialkylfluorosilanes (see Table) without use of anhydrous hydrogen fluoride, working with which is, of course, very inconvenient. We carried out reaction between hexaalkyldisiloxanes and potassium or ammonium hydrogen fluoride in sulfuric acid:

$$R_3SiOSiR_3 + KHF_2 + H_2SO_4 \xrightarrow{-H_2O} 2R_3SiF + KHSO_4$$

As these acid fluorides contain 16-17% more fluorine than the corresponding neutral fluorides, correspondingly less used, which makes the synthesis of trialkylfluorosilanes more economical.

The synthesis was carried out by adding the potassium or ammonium hydrogen fluoride to a stirred solution of hexaalkyldisiloxane• in sulfuric acid cooled to 0°. The trialkylfluorosilane formed was distilled directly from the reaction mixture at ordinary or reduced pressure, or it was separated and then purified by distillation. Yields of 85-88 % were obtained.

EXPERIMENTAL

Fluorotrimethylsilane. One mole (162 g) of hexamethyldisiloxane, b.p. 100.3° (760 mm), was added slowly to 350-450 ml of concentrated sulfuric acid at 0° contained in a three-necked round-bottomed flask fitted with mercury-sealed mechanical stirrer and a condenser set for distillation. Dry potassium hydrogen fluoride (117 g, i.e. 1.5 moles) was then added in small portions to the stirred cooled sulfuric acid solution, after which the solution was stirred with cooling for a further ten minutes. The mixture was then heated in a water bath, and the fluorotrimethylsilane that distilled off was collected in a trap cooled to − 75°. After being freed from traces of hydrogen fluoride by distillation over anhydrous potassium fluoride, 156.5 g (85%) of fluorotrimethylsilane, b.p. 16-17°, was obtained.

Triethylfluorosilane. Potassium hydrogen fluoride (11.9 g, i.e. 0.15 mole) was added to a stirred solution of 24.7 g (0.1 mole) hexaethyldisiloxane, b.p. 236.3° (760 mm) in 50 ml of sulfuric acid at 0°. The mixture was then stirred with cooling for a further ten minutes and at room temperature for 30 minutes. The upper layer was separated, and the lower layer was extracted with petroleum ether of b.p. 28-38°. Solvent was distilled off, and distillation of the residue through a column gave 22.8 g (85%) of triethylfluorosilane, b.p. 109-111°.

Fluorotripropylsilane and tributylfluorosilane were prepared similarly. The physical constants of the trialkylfluorosilanes obtained (after purification from traces of hydrogen fluoride by treatment with anhydrous potassium fluoride and redistillation through a column), their yields, and analysis [4] are given in the table.

It must be pointed out that these constants differ considerably from those given in the literature [5] and in reference books, and they are more reliable. We give here the Raman spectra of $(C_2H_5)_3Si\,F$ and $(n\text{-}C_4H_9)_3SiF$.••

SUMMARY

Four trialkylfluorosilanes were prepared by the action of potassium or ammonium hydrogen fluoride on solutions of hexaalkyldisiloxanes in sulfuric acid. Their physical properties and Raman spectra are described.

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• The hexaalkyldisiloxanes were synthesized by reaction of the corresponding alkylmagnesium chlorides with hexachlorodisiloxane [3].

•• The Raman spectra were kindly determined by V. A. Kolesova.

••• [See C. B. translation].

SEPARATION OF CERTAIN CATIONS FROM FERRIC IONS ON OXYCELLULOSES

V. I. Ivanov, N. Ya. Lenshina, and V. S. Ivanova

In previous investigations we showed that oxycelluloses are able to absorb ferric ions selectively [1, 2]. This is confirmed by the fact that elution of iron from oxycellulose requires an acid solution of higher concentration than that required for other cations investigated. We have applied this property to the separation of a mixture of ferric ions and any other cation.

EXPERIMENTAL

The experimental procedure was as described previously [1]. The volume of mixed solution taken was 100 ml. The amount of oxycellulose (12.2% COOH, exchange power 2.7 mg-equiv/g) taken was that calculated to give complete sorption of ferric ions. The filtrates were analyzed for contents of cations by the appropriate colorimetric methods (thiocyanate, dimethylglyoxime, dithizone) [3]. The results on the separation of nickel and zinc from ferric iron are given in Table 1.

TABLE 1

Results on the Separation of Ni^{2+} and Zn^{2+} from Fe^{3+}.

No.	Mixture to be separated, Fe^{3+}/X^{2+} *	Amount of oxycellulose taken (g)	Amounts of Fe^{3+} and X^{2+} (mg)	Amount of X^{2+} found in the filtrate (mg)	Fe^{3+} content of filtrate
1	Fe^{+3}/Ni^{+2}	2	50+50	49.0	None
2	Fe^{+3}/Ni^{+2}	2	50+50	50.0	"
3	Fe^{+3}/Ni^{+2}	0.5	5+50	29.5	"
4	Fe^{+3}/Zn^{+2}	2	50+50	48.0	"
5	Fe^{+3}/Zn^{+2}	2	50+50	48.5	"
6	Fe^{+3}/Zn^{+2}	0.5	5+50	49.1	"

* X^{2+} is a bivalent cation.

We used the same procedure in experiments on the quantitative separation of ferric iron from other cations. The results are given in Table 2.

Traces of the second cation remaining on the oxycellulose may be eluted with 0.01 N HCl without washing out any iron. Hence, this method can be extended to the separation of Fe^{3+} from other cations.

Separation of the cations was based on our observations on the dependence of sorption of the ions on the pH of the medium. We showed that Fe^{3+} is completely sorbed at a pH of about 2, Cu^{2+} at a pH of about 5, and Ni^{2+} at a pH of about 6. Hence, the strength of the bonds between the ions and oxycellulose in an acid medium increases along the series Ni^{2+}, Cu^{2+}, and Fe^{3+}. The pH values at which sorption of the cations is complete are close to those at which the metal hydroxides are precipitated (Table 3).

TABLE 2

Separation of Ferric Iron from Certain Cations (Weight of oxycellulose 2 g; original mixture of cations – 50 mg of Fe^{3+} and 50 mg of X^{2+} or X^{3+}).

No.	Mixture to be separated	Test for Fe^{3+} in filtrate	Fe^{3+} content of eluate
1	Fe^{+3}/Co^{+2}	Negative	49.8
2	Fe^{+3}/Cu^{+2}	"	49.5
3	Fe^{+3}/Pb^{+2}	"	50.0
4	Fe^{+3}/Sr^{+2}	"	50.1
5	Fe^{+3}/Mg^{+2}	"	9.2
6	Fe^{+3}/Ca^{+2}	"	49.0
7	Fe^{+3}/Ba^{+2}	"	50.0
8	Fe^{+3}/Al^{+3}	"	49.5

TABLE 3

Comparison Between pH for Sorption of Cations and pH for Precipitation of their Hydroxides.

Cation	pH for sorption	pH for precipitation of hydroxide
Ni^{+2}	6	7-8
Cu^{+2}	4.7	5
Fe^{+3}	1.8	2-3

On this basis predictions may be made concerning the possibility of separating cations. The method described can be used for the separation of other cations.

SUMMARY

1. The separation of Ni, Co, Cu, Zn, Pb, Sr, Mg, Ca, Ba, and Al ions from ferric ions was effected quantitatively on oxycellulose as sorbent.

2. It was observed that the pH of the solution from which a given ion is completely absorbed by oxycellulose is close to that for the precipitation of the corresponding hydroxide, and this fact can serve as a guide in the separation of ions.

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* [See C. B. translation].

** [In Russian].

TRANSFORMATIONS OF CELLULOSE AT ELEVATED TEMPERATURES

COMMUNICATION 4. EFFECT OF THE DEGREE OF POLYMERIZATION OF CELLULOSE ON THE FORMATION OF LEVOGLUCOSAN

O. P. Golova, A. M. Pakhomov, and I. I. Nikolaeva

In considering the various properties of cellulose, we must always keep in mind its two main properties as a polymeric compound: the chain length of the macromolecule (degree of polymerization) and the supermolecular structure of the cellulose preparation (density of packing of the macromolecules). The study of the transformations of cellulose in a heterogeneous medium meets difficulties with respect to the obtaining of exact data on the effects of these two properties. Other factors often affect the course of reaction, e.g. accessibility to reagent, its tendency to be adsorbed, and the nature of the solvent or medium. Investigation of the transformations of cellulose in the solid state, i.e. the thermal decomposition of cellulose, makes it possible to characterize the part played by the chain length of the molecule, since in this case the effect of the liquid phase and the complicating effects of the above-mentioned factors are eliminated. We have already [1] considered the effect of the structure of cellulose (density of packing) on the formation of levoglucosan (1,6-anhydro-β-D-glucopyranose).

In the present paper we give results of an investigation of the effect of degree of polymerization on yield of levoglucosan, as the main primary product of the thermal decomposition of cellulose in a vacuum, and we give also results of an investigation of the effect of reduction of the chain length to the minimum (disaccharide) on the formation of levoglucosan. Investigations on the formation of levoglucosan from a monosaccharide (β-D-glucose), trisaccharide, pentasaccharide, etc. will be published separately.

We used cellulose samples varying in degree of polymerization from 1000 to 150, but having identical supermolecular structures (identical degree of packing of macromolecules). The work was carried out with cotton cellulose purified by the standard method of Corey and Gray and then treated for various periods with dilute acid. The cellulose samples obtained were characterized by degree of polymerization and contents of carbonyl (determined by the hydroxylamine method) and carboxy groups (determined by the calcium acetate method).

As is well known, in the hydrolysis of cellulose in a weakly acid medium the rate of reaction becomes constant after an initial period [2]. The samples were therefore taken after this period of hydrolysis. Determination of sorption-desorption curves for some of the samples showed that the curves were identical and the samples all had the same hydrolyzability. These characteristics of the cellulose preparations indicate constant density of packing.

The cellulose samples were heated in a vacuum under optimum conditions for the formation of levoglucosan. The process of thermal decomposition of cellulose was characterized by the yield of technical levoglucosan (pastelike distillate), readily volatile substances (frozen out in traps by liquid nitrogen), and dry residue. The technical levoglucosan was analyzed for levoglucosan content, which was determined from the increase in the amount of reducing substances after hydrolysis of the solid distillate. The experimental results are given in the table. Change in the degree of polymerization of the cellulose from 1000 to 150 (1000, 450, 200, 150) had no effect on the formation of levoglucosan, which was obtained in 59-63% yield.

TABLE

Effect of Degree of Polymerization of Cellulose on Yield of Levoglucosan.

Degree of polymerization	Number of functional groups per 100 glucose residues		Yield of thermodecomposition products (% on cellulose taken)		Dry residue	Composition of solid distillate		Yield of levoglucosan (% on cellulose taken)
						Reducing substances		
	CHO groups	Total COOH groups	Solid distillate	Fraction frozen out by liquid nitrogen		Before hydrolysis	After hydrolysis	
1000	0.510	0.144	78	15	4.8	6.0	96.0	63.0
450	0.530	0.144	72	18	5.6	13.7	94.0	59.0
200	0.638	0.144	76	18	4.8	13.0	93.0	61.0
190	0.748	0.144	74	19	6.6	12.0	92.6	60.0
150	0.928	0.144	75	15	5.9	11.3	91.8	60.0

In order to determine the effect of reducing chain length to a minimum on the formation of levoglucosan, we investigated the thermal treatment of cellobiose in a vacuum under the conditions used for cellulose. Work on the thermodecomposition of cellobiose has been carried out by Puddington [3], who heated it at 210-240° at 10^{-4} mm and followed the course of the process from the rise in the amounts of H_2O, CO, and CO_2. Puddington concluded that no levoglucosan is formed in this process.

Our investigations showed that in the thermal treatment of cellobiose in a vacuum a sirupy distillate (25% yield) is formed. This contains about 60% of reducing substances and the increase in the amount of reducing substances after hydrolysis is only 12%. If we associate this increase with the formation of levoglucosan, then the yield of levoglucosan can be only 3.5% on the cellobiose taken. We must point out that the sirupy disillate did not crystallize after two years in a vacuum desiccator in spite of seeding with crystalline levoglucosan.

SUMMARY

1. Change in the chain length of cellulose from 1000 to 150 glucose residues with preservation of the physical structure of the cellulose has no effect on the yield of levoglucosan, which amounts to 59-63%.

2. A chain length of two glucose residues (cellobiose) does not permit appreciable formation of levoglucosan.

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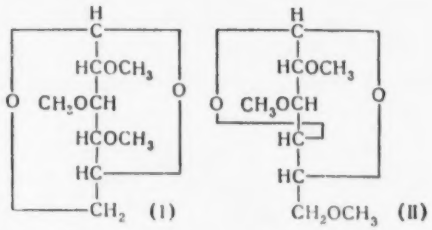
* [See C. B. translation].

THERMAL DEGRADATION OF TRIMETHYLCELLULOSE IN A VACUUM

A. M. Pakhomov, O. P. Golova, and I. I. Nikolaeva

The first attempt at a study of the thermal degradation of cellulose ethers in a vacuum was made by Hess and Wittelsbach [1], who used ethylcellulose for this purpose. However, in view of the low yield of degradation products, these authors did not continue the investigation. Almost simultaneously Reiley [2] examined the thermal degradation of dimethyl- and trimethyl-celluloses; he stated that he obtained dimethyl- and trimethyl levoglucosans, but he did not establish the positions of the anhydride bridges in these compounds.

In the thermal degradation of trimethylcellulose in a vacuum it would be expected that the 1,4-glucosidic link would be broken with possible formation of 2,3,6-tri-O-methyl-1,4anhydro-β-D-glucopyranose (II). Reiley's statement concerning the formation of 2,3,4-tri-O-methyl-1,6-anhydro-β-D-glucopyranose (trimethyllevoglucosan) (I) under these conditions requires confirmation.



According to Reiley, the thermal degradation of trimethylcellulose to trimethyllevoglucosan is merely depolymerization. According to modern views on the structure of cellulose, for the formation of trimethyllevoglucosan from trimethylcellulose, a subsequent isomerization is necessary, which we consider to be unlikely. This isomerization must consist in the transfer of the methyl of 6-methoxy to 4-hydroxy.

The determination of the possibility of the formation of these anhydrides in the thermal degradation of trimethylcellulose in a vacuum is of considerable interest. The identification of 2,3,6-tri-O-methyl-1,4-anhydro-β-D-glucopyranose among the thermodegradation products of trimethylcellulose would confirm the view that blocking of the hydroxy groups by etherification leads to stabilization of the product arising from the breaking of 1,4-glucosidic links. On the other hand, establishment of the presence of trimethylglucosan would indicate that the fragment of the trimethylcellulose molecule formed by rupture of the glucosidic link can undergo isomerization.

In order to elucidate these matters and so reject or confirm Reiley's statement, we investigated the thermal degradation of trimethylcellulose in a vacuum and determined the structure of the glucose anhydride formed.

EXPERIMENTAL

The trimethylcellulose that we used was prepared by transetherification of the secondary acetate. It was subjected to thermal degradation under the optimum conditions for the formation of levoglucosan from

cellulose. The pastelike product of thermal degradation was collected in the form of two fractions. The first fraction (33% of the total weight of distillate) was a colorless sirupy substance. The second fraction (67%) was darker in color and was solid at room temperature. Analytical results for the products are given in the table.

TABLE

OCH_3 content of trimethylcellulose (%)	Yield (% on trimethylcellulose taken) of		OCH_3 content (%) of	
	Pastelike distillate	Undistilled dry residue	Light-colored fraction	Dark-colored fraction
44.6•	71.0	4.5	39.0	42.0

• Completely etherified cellulose should contain 45.6% methoxy groups.

For the purification of the pyrolysis products of trimethylcellulose we first used distillation in a high vacuum (10^{-5} mm), as recommended in the literature for the purification of carbohydrate ethers [3]. It was found, however, that distillation of the thermodegradation product of trimethylcellulose was accompanied by considerable degradation. Purification of the thermodegradation products by high-vacuum fractionation was therefore abandoned.

For the identification of the thermodegradation products we used the method proposed by Robertson [4] for the separation of 2,3,4- and 2,3,6-trimethylglucoses. This method consists in conversion of the corresponding glucosides and their separation by taking advantage of differences in solubility. The two fractions of the thermodegradation product of trimethylcellulose (dark-colored and light-colored) were investigated separately.

By hydrolysis with dilute hydrochloric acid the second (dark-colored) fraction was converted into a mixture of the corresponding glucoses. The aqueous solution was neutralized with barium carbonate and evaporated to dryness under reduced pressure. The dry residue was ground and extracted several times with chloroform. The chloroform extract was evaporated under reduced pressure, and after being kept in a vacuum desiccator the residue crystallized out partially. We did not succeed in isolating the crystals in a pure state. The partially crystallized product, which was obtained in 64% yield (based on the original amount of trimethylglucose anhydride), was dissolved in absolute methanol, and the solution was saturated with dry hydrogen chloride gas in order to give the corresponding methyl glucosides. The reaction mixture was heated in a water bath and then evaporated down to constant weight under reduced pressure. The sirupy residue (76% yield calculated on trimethylglucose) was dissolved in the least possible amount of water and repeatedly extracted with chloroform. If both methyl glucosides were present in the reaction product, it would be expected that methyl 2,3,6-trimethylglucoside would pass into the chloroform, whereas methyl 2,3,4-trimethylglucoside would remain in the aqueous solution.

The chloroform solution was evaporated to dryness under reduced pressure and the residue – a yellow sirup – was hydrolyzed to the trimethylglucose. The residue remaining after evaporation solidified completely; yield 70.5%. After crystallization from dry ether it melted at 112-115°. 2,3,6-Trimethylglucose has the same melting point (112-115°). The aqueous solution was also evaporated under reduced pressure, and the very small residue was hydrolyzed to the trimethylglucose. After being recrystallized from dry ether this substance also melted at 112-115°.

According to the literature [4], 2,3,4-trimethylglucose is a sirup. In presence of 2,3,4-trimethylglucose, 2,3,6-trimethylglucose will not crystallize. As the hydrolysis product from the methyl glucosides contained in the chloroform and aqueous solutions solidified completely after evaporation of solvents, it may be considered that the dark-colored fraction of the pyrolysis products of trimethylcellulose does not contain 2,3,4-tri-O-methyl-

1,6-anhydro-β-D-glucopyranose, i.e. trimethyllevoglucosan.

In the investigation of the light-colored fraction of the pyrolysis products of trimethylcellulose by the above-described method, immediately after the first stage (hydrolysis) we obtained snow-white crystals of 2,3,6-trimethylglucose, m.p. 110-114°; yield 80 %. This indicates that the light-colored fraction of the pyrolysis products of trimethylcellulose also does not contain 2,3,4-tri-O-methyl-1,6-anhydro-β-D-glucopyranose, which would have been converted into 2,3,4-trimethylglucose in the course of the above-described treatment.

Our results, therefore, are in conflict with Reiley's statement that the trimethylanhydroglucose obtained in the thermal degradation of trimethylcellulose in a vacuum is trimethyllevoglucosan. The trimethylanhydroglucose that we obtained was 2,3,6-tri-O-methyl-1,4-anhydro-β-D-glucopyranose, the formation of which must result from rupture of 1,4-glucosidic links without subsequent isomerization.

SUMMARY

1. A study was made of the thermal degradation of trimethylcellulose in a vacuum. It was shown that 2,3,6-tri-O-methyl-1,4-anhydro-β-D-glucopyranose was present in the degradation products.

2. Statements in the literature regarding the formation of 2,3,4-tri-O-methyl-1,6-anhydro-β-D-glucopyranose under these conditions were not confirmed.

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